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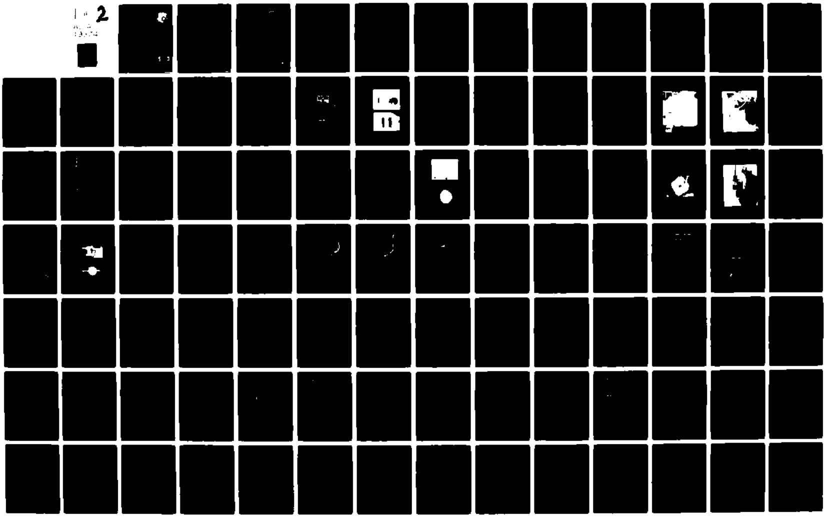

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TESTING OF AN IMPROVED LITHIUM-SULFUR DIOXIDE BATTERY FOR AIRCREW LIFE SUPPORT EQUIPMENT

James S. Cloyd
Aerospace Power Division

May 1982

Final Report for Period January 1979 - October 1981

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This technical report has been reviewed and is approved for publication.

James S. Cloyd

JAMES S. CLOYD
Project Engineer

Donald P. Mortel

DONALD P. MORTEL
Technical Area Manager

FOR THE COMMANDER

J D Reams

JAMES D. REAMS
Chief, Aerospace Power Division

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This report presents the results of in-house testing of lithium-sulfur dioxide cells, manufactured by Honeywell Power Sources Center, Horsham, PA. These cells were representative of the manufacturing technology developed under a Materials Laboratory sponsored program entitled "Manufacturing Methods for Lithium Batteries" under AF Contract No. F33615-76-C-5261. The report includes performance testing of an engineering prototype design of lithium-sulfur dioxide cells and the performance characterization, storage evaluations (cont'd)

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and abuse test behavior of the pilot production cell design. Several design modifications occurred during the development of this lithium-sulfur dioxide cell technology which significantly changed their performance.

Testing of the pilot production cells included: (1) Performance evaluations at rates of 50MA, 100MA, 200MA, and 400 MA at temperatures from -65°F to +140°F; (2) Room temperature discharge tests at high rates of current; (3) Capacity retention capability as a function of storage time at temperatures of 32°F, 70°F and 160°F; (4) Evaluation of intermittent storage capability at 205°F, and (5) Abuse testing. Abuse testing included short circuit, nail penetration, and forced overdischarge conditions.

It was determined that the design modifications made to these cells collectively contributed to provide a lithium-sulfur dioxide cell with enhanced low temperature and high discharge rate performance as well as improved behavior under abuse conditions.

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FOREWORD

This report contains the results of testing a lithium-sulfur dioxide pilot production lot of cells produced by Honeywell Power Sources Center, Horsham PA under the direction of the Materials Laboratory, WPAFB, Ohio 45433. The test and evaluation was performed by AFWAL/POOC-1 of the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson AFB, Ohio. This work was sponsored by the Aeronautical Systems Division Life Support Systems Project Office under Project No. 412A and Job Order No. ASDAELS1. This effort was conducted by James S. Cloyd, AFWAL/POOC-1. Technical support was provided by I. F. Luke, AFWAL/POOC-1. All testing was performed by Charles T. Napier and Marvin Gaston, AFWAL/POFP. These tests were conducted during the period January 1979 - December 1980. This report contains the initial data from various on-going tests on this cell technology. These tests will continue and subsequent reports will be published to report this additional data.

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SECTION I

INTRODUCTION

Air Force requirements for the operation of many Life Support/Aircrew Survival Equipment applications dictate the need for a reliable, durable battery as the power source. With the need for military readiness under austere conditions, rigorous operational requirements, such as mandatory low temperature operation are placed on these batteries. In some Aircrew Survival Radio applications the successful location and rescue of Aircrew members can be directly attributed to the operation of the battery. As a result, the requirements for batteries have stressed long operating life over an extreme range of temperatures and minimum weight and volume.

Until recently most of the Life Support Equipment incorporating primary, nonrechargeable cells or batteries have used the zinc-manganese dioxide or zinc-mercuric oxide electrochemical systems. The zinc-manganese dioxide system displays a steadily decreasing voltage during discharge and exhibits energy densities of 40-45 watt/hours/pound and 3.5-3.9 watt-hours/cubic inch. The zinc-mercuric oxide system provides a relatively flat voltage curve during discharge at energy densities of 50-55 watt-hours/pound and 6.0-6.4 watt-hours/cubic inch. Both of these systems contain an aqueous electrolyte system and therefore have difficulty providing power at temperatures below 0°C. As a result of these shortcomings, the use of lithium batteries has become an increasingly attractive alternative as a power source for numerous Air Force applications.

Lithium batteries were, in the early 1970's, a relatively new technology, and early work indicated that these batteries could provide highly substantial improvements in the areas of voltage per cell, available capacity, low temperature performance, storage life capability, and energy densities. The development of several new electrochemical couples incorporating lithium as the anode material was initiated and one of the most promising new couples was the Lithium-Sulfur Dioxide System ($Li-SO_2$).

As these new lithium technologies were emerging, a new Tri-Service Survival Radio System, designated the AN/PRC-112, was being developed which had requirements for low weight, minimum volume, low cost, and most importantly, operation at extreme low temperature (at least -40°C). Life Support Equipment had typically been unable to function in certain austere environments due to constraints in battery operational capability below 32° to 0°F. Because of the desire to incorporate improved battery technology in the Advanced Survival Radio, the Lithium-Sulfur Dioxide Battery was tentatively chosen to power the new system. However, since this electrochemical couple was developmental in nature, a need existed to develop mass production capabilities for the Li-SO_2 cell.

To fulfill this need, the Air Force Materials Laboratory, Wright-Patterson AFB, Ohio established, in 1976, a Manufacturing Methods Technology Program with Honeywell Power Sources Center (HPSC), Horsham PA. The objective of this program was to assess the manufacturability of Li-SO_2 cells and to scale up their facilities to fabricate Li-SO_2 cells at a production rate.

As a result of the known unsafe behavior of this technology under certain abusive conditions, the Air Force desired a cell with significantly improved safety capabilities. To attain the safest possible cell, several parameters of the Li-SO_2 system were studied by HPSC and modifications were made to the cell design and component compositions through a series of cell fabrication/testing steps. During the MMT program there were four iterations of cells fabricated; there were designated baseling performance cell (BPC), first engineering prototype cell (first EPC), second engineering prototype cell (second EPC), and pilot production cell (PPC).

Under the terms of the Manufacturing Methods Contract, a quantity of first EPC cells each of four different cell sizes (AA, A, C, and 0.5D) were delivered to the Aero Propulsion Laboratory (APL), Wright-Patterson AFB, Ohio in early 1978. These cells were delivered in order that the Air Force could evaluate the performance of the first EPC design and to establish baseline data for comparison with later designs. A detailed description of the first EPC Li-SO_2 design is given to Appendix A to this report.

Due to PRC-112 survival radio volume constraints and the need for 24 hours of continuous operation, it was determined that the 0.5D size cell configuration would most effectively fulfill the radio battery requirements. This cell was designated the 0.5D configuration because it has the same diameter as the standard ANSI "D" size cell and is approximately one half the height of the standard "D" cell configuration. The detailed description of the first EPC design as given in Appendix A is specifically for the 0.5D cell size. The results of the in-house testing of the first EPC design are also provided in Appendix A to this report and will be discussed in greater detail in Section V, Conclusions. Only the 0.5D cell of the first engineering prototypes was tested at APL.

It was determined that the PRC-112 survival radio required the capability to withstand intermittent nonoperating exposure to 205°F. This requirement was realized as the result of a study which showed that a maximum temperature of 205°F could be obtained in the cockpit on an aircraft. This extreme temperature is caused by a greenhouse effect through the canopy when exposed to direct sunlight. This phenomenon is extremely severe and state of the art Li-SO_2 technology was unable to withstand such temperatures without hydraulically venting and becoming inoperative. As a result, Honeywell (HPSC) modified the cell design to increase the capability of the Li-SO_2 system to withstand intermittent storage temperatures of up to 205°F. This modification consisted of increasing the cell height (and therefore volume) while leaving the cell contents at the levels of the shorter design cell. This allowed for increased volume for internal components to expand at high temperatures without reaching the burst pressure of the vent mechanism. Henceforth, the cell was designated the "0.6D" cell configuration. This design feature was incorporated in both the second EPC design and in the pilot production cell design, and a discussion of its effectiveness and impact on cell volumetric energy density is given in Section V.

Another design feature in the pilot production cell for potentially improved safety and disposability, was the incorporation of an expanded nickel grid as a current collector in the lithium anode. This feature was included at the recommendation of the Air Force and as a result of investigations done under the manufacturing methods program. It was shown that lithium utilization was improved with the use of a grid when compared to a diagonal strip across the anode surface or to the use of the lithium anode with no added current collector. A discussion of the effects on performance of the use of a grid current collector is given in Section V.

In the same time frame as the Manufacturing Methods Program, studies sponsored by the Army (References 1, 2) indicated that the ratio of active materials or more specifically the lithium to sulfur dioxide (SO_2) ratio had a significant effect on the safety characteristics of the cell under abuse conditions. Their findings and the work done at HPSC indicated that a cell in which the lithium to SO_2 ratio is 0.9 to 1.10 would demonstrate superior safety over a cell containing excess lithium (i.e., lithium to SO_2 ratio of 1.1 to 1.5). It will be shown that this basic design modification under the MMT program produced highly significant changes in cell capacity. It was hoped, that the lithium limited cell would also be more acceptable for final disposal to the environment, since it is presumed that virtually all lithium is consumed during cell discharge.

SECTION II

DESCRIPTION OF CELLS

The physical characteristics of the first engineering prototype cell design are reported in Appendix A, "Evaluation of Prototype Lithium-Sulfur Dioxide Cells", which is included at the end of this report. The physical characteristics of the pilot production cell are given in Table 1. For purposes of discussion, detailed comparative data on the two cell designs is given in Table 2. This table contains the specific physical characteristics of both the first EPC design and pilot production cell which represent design and component modifications made to the cell during the manufacturing methods program. A cross-sectional view of the pilot production cell is given in Figure 1.

The key physical features of the pilot production cell are:

1) Lithium limited cell capacity

2) Increased void volume in the cell to allow for electrolyte exapnsion during high temperature exposure

3) Decreased Teflon concentration in the carbon cathode structure

4) Extra drying steps performed during manufacture

5) Incorporation of an expanded nickel grid as a current collector in the lithium anode

A comparative photograph of the vent mechanisms of both the first EPC (on the left) and the pilot production cell (on the right) is shown in Figure 2a. Figure 2b is a photograph of the pilot production cell.

TABLE 1

PHYSICAL CHARACTERISTICS OF 0.6 "D" CELL

PILOT PRODUCTION

PHYSICAL	
Outside diameter	1.324 in.
Length (nom.)	1.427
Volume	1.98 $in.^3$
Weight	58 gms.
Case thickness	0.017 in.
ELECTRODES	
Cathode	
Length	28 in.
Width	.92 in.
Thickness	.03 in.
Mix weight	4.25 gms.
Cathode area	332 cm^2
Anode	
Grid (nickel metal) weight	2.0 gms.
Length	24.5 in.
Width	.92 in.
Thickness	.0070 in.
Weight	1.33 gms.
Capacity	5.14 AH
Separator	
Length (avg.)	28.9 in.
Width	1.125 in.
Weight	2.0 gms.
Electrolyte (64.4 Wt. % SO_2)	
Volume	16.4 cc
Theoretical capacity	5.5 AH

TABLE 2

COMPARISON OF PHYSICAL CHARACTERISTICS

(FIRST ENGINEERING PROTOTYPE VS. PILOT PRODUCTION)

	1st EPC	PRODUCTION
PHYSICAL		
Length	1.190 in	1.427 in
Weight	47.8 g	58 g
Volume	1.64 in^3	1.98 in^3
CATHODE		
Carbon/Teflon	80/20	95/5
Length	16.00 in	28.0 in
Width	0.65 in	0.92 in
Thickness	0.016 in	0.03 in
Area	134 cm^2	332 cm^2
Drying Conditions	No Heat Treatment	Heat Treatment (Additional Dryin
ELECTROLYTE		
Composition	72.0 wt. % SO_2	64.4 wt. % SO_2
Volume	15.0 cm^3	16.4 cm^3
Theoretical Capacity	5.7 AH	5.5 AH
ANODE		
Theoretical Capacity	6.50 AH	5.14 AH
Current Collector	No Grid	Nickel Grid

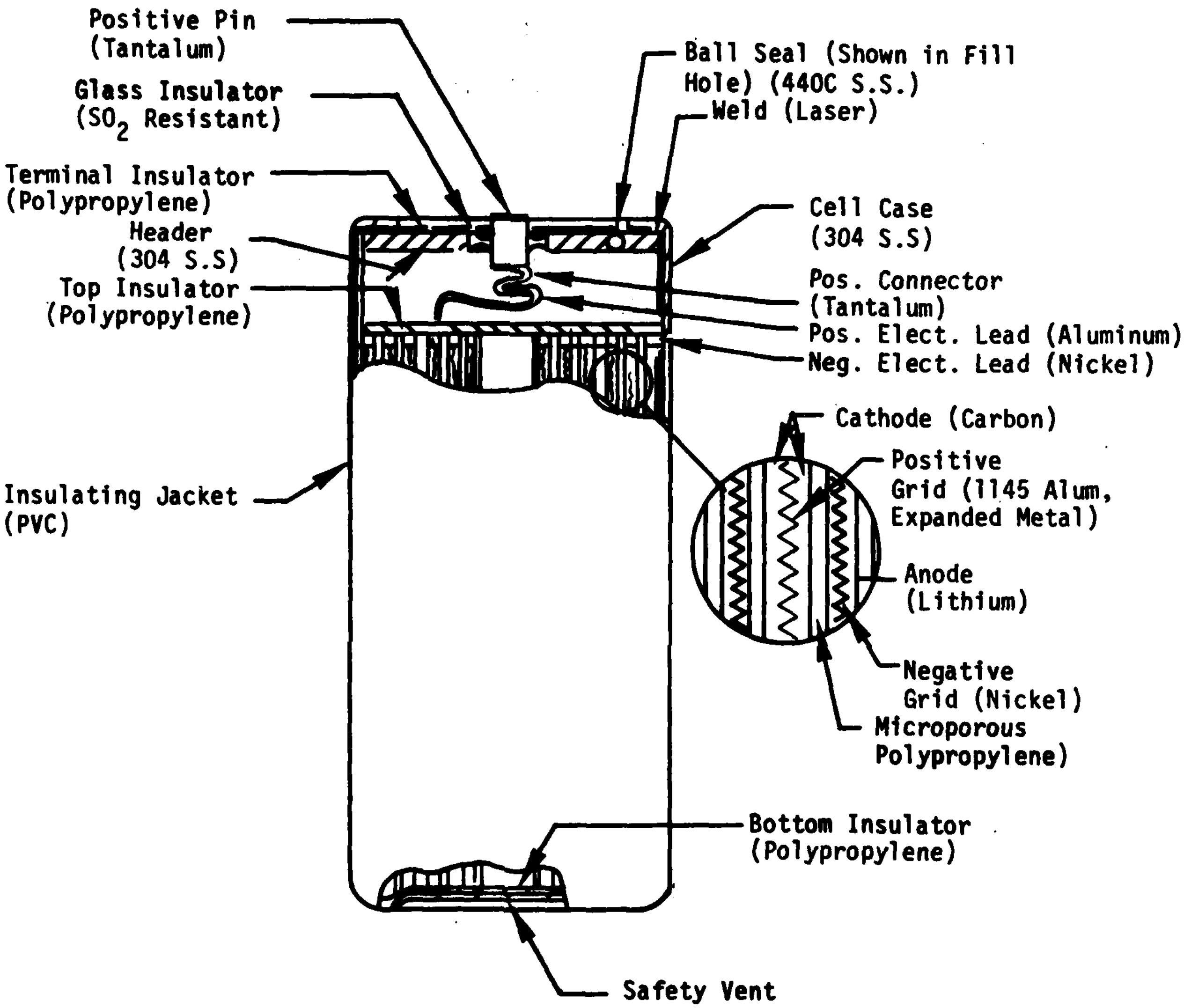

Figure 1. Cross-Sectional View of the Pilot Production Cell

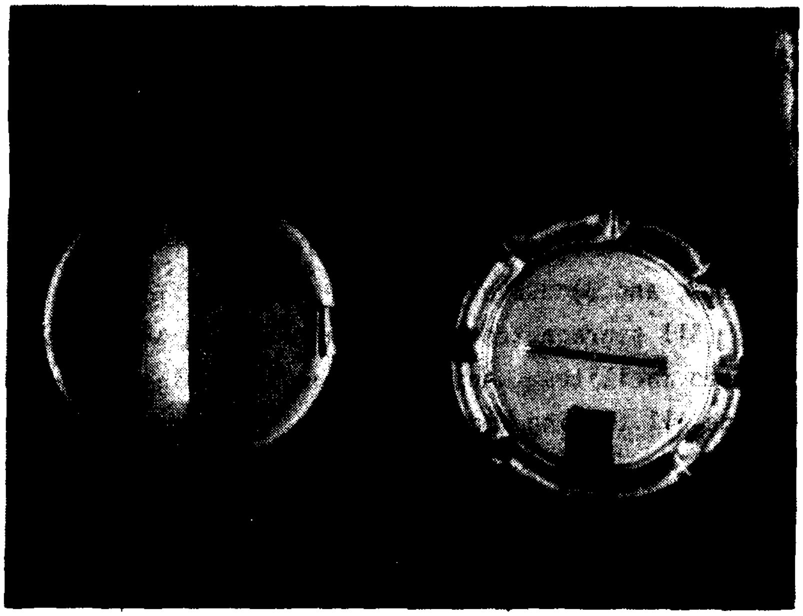

Figure 2a) Vent Mechanism of the First EPC and the Pilot Production Cell;

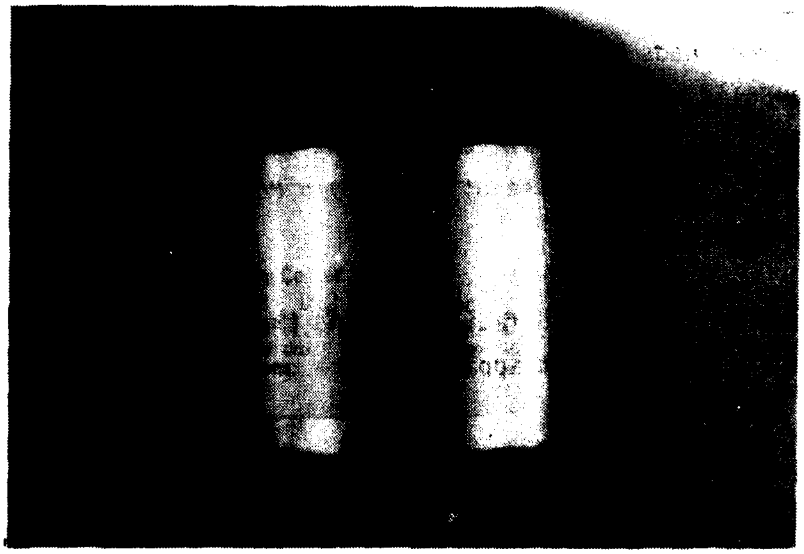

Figure 2b) Pilot Production Cell

SECTION III

TEST PROCEDURES AND FACILITIES

A summary of the test conditions and the number of cells used for each test is given in Table 3.

General safety consideration taken for these tests included: 1) Use of an automatic 2.0 volt end-of-discharge voltage cut-off for cell discharges, 2) Use of a specially vented environmental chamber for all cell discharge tests, and 3) Use of a remote test site for all hazardous, abusive testing. All storage tests were performed in locked, well ventilated, isolated facilites. Appropriate warning signs and labels were placed outside all testing facilities.

Data collection was accomplished through the use of a Hewlett-Packard Model 2100A Computer. Strip chart recordings were also obtained for back-up data through the use of a Texas Instrument Servo-Writer II Strip Chart Recorder.

All discharge loads for these tests were constant current loads generated by a Solid State Load Bank constructed at the Aero Propulsion Laboratory (APL). All testing at temperatures other than room temperature were accomplished through the use of a Tenney 5 Model No. T5-110350 Environmental Chamber.

Photographs of the storage facilities and the abuse test facilities, with the external short circuit apparatus, are provided as Figures 3 and 4.

Figure 5 shows the position used for thermocouple placement during the four cell series connected battery testing.

TABLE 3

SUMMARY OF TEST CONDITIONS
(PILOT PRODUCTION CELL)

NAME OF TEST	TEST DISCRIPTION/CONDITIONS	NO. OF CELLS EVALUATED PER CONDITION
ROOM TEMPERATURE STORAGE VS. CAPACITY RETENTION TEST	Room ambient, upright position storage followed by cell discharge at 300MA constant current at room temperature to a 2.0 v end-of-charge voltage at intervals of 0,1,2,3,6,9,12,18,24,30, 36,42,48,54, and 60 months	Six cells per each designated month of storage (Total = 96 cells)
HIGH TEMPERATURE STORAGE VS. CAPACITY RETENTION TEST	160^{o}F, upright position storage followed by cell discharge at 300MA constant current at room temperature and -40^{o}F to a 2.0 volt end-of-discharge voltage at intervals of 1,2,3,4,5,6,7,8 and 9 months	Six cells per inch designated month of storage for each temperature (Total = 54 cells)
LOW TEMPERATURE STORAGE VS. CAPACITY RETENTION TEST	32^{o}F, upright position storage followed by cell discharge at 300MA constant current at room temperature to a 2.0 volt end-of-discharge voltage at intervals of 6,12,18,24,30,36,42,48,54, and 60 months of storage	Six cells per designated month of storage (Total = 60 cells)

TABLE 3 (CONT'D)

NAME OF TEST	TEST DESCRIPTION/CONDITIONS	NO. OF CELLS EVALUATED PER CONDITION
FRESH CELL PERFORMANCE UNDER PRC-112 RADIO LOADS AT VARIOUS TEMPERATURES TEST	Discharge two each four cell battery packs at radio load at temperatures of -40^0F, -20^0F, 0^0F, 70^0F, 100^0F, 120^0F, and 160^0F.	Two each four cell series connected strings, strapped together to form a square with one cell at each corner of the square, per each temperature. (Total = 56 cells)
FRESH PERFORMANCE EVALUATION TEST	Discharge cells under constant current loads of 50, 100, 200, and 400MA at temperatures of -65^0F, -40^0F, 0^0F, 30^0F, 70^0F, 100^0F, and 140^0F to a 2.0 volt end-of-discharge voltage	Four cells per each temperature/load condition (Total =112 cells)
HIGH RATE DISCHARGE TEST	Discharge fresh cells at rates of 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 amperes at room temperature	Two cells each at each rate of discharge (Total = 16 cells)
SEAL EVALUATION TEST	Daily temperature cycling at 160^0F (two hours), 205^0F (one hour), and 160^0F (two hours) followed by constant current discharge at 300MA at room temperature to a 2.0 volt end-of-discharge voltage. Discharge cells at 1,2,3, and 4 weeks of temperature cycling exposure.	Four "Standard" seal cells and one "New" seal cell per each week of temperature cycling (Total = 20 cells)

TABLE 3 (CONT'D)

NAME OF TEST	TEST DESCRIPTION/CONDITIONS	NO. OF CELLS EVALUATED PER CONDITION
ABUSE TEST	EXTERNAL SHORT CIRCUIT: Fresh cells under maximum load of 0.03Ω at room temperature and at $^-40^0$F. Fresh batteries under maximum load of 0.03Ω at room temperature and at $^-40^0$F.	EXTERNAL SHORT CIRCUIT: Two fresh cells per temperature condition. One each four cell series string per temperature condition. (Total = 12 cells)
	INTERNAL SHORT CIRCUIT: Puncture fresh cells with a nail and leave nail in the cell at room temperature and $^-40^0$F.	INTERNAL SHORT CIRCUIT: Two cells per each temperature condition (Total = 4 cells)
	FORCED OVERDISCHARGE: Force overdischarge of discharged cells (2.0 volt end-of-discharge voltage) for a time equivalent to 100% of rated cell capacity after 0.0 volts. Overdischarge at rates of 300MA, 1000MA, and 2000MA at room temperature and $^-40^0$F.	FORCED OVERDISCHARGE: Two cells per each rate and temperature condition (Total = 12 cells)

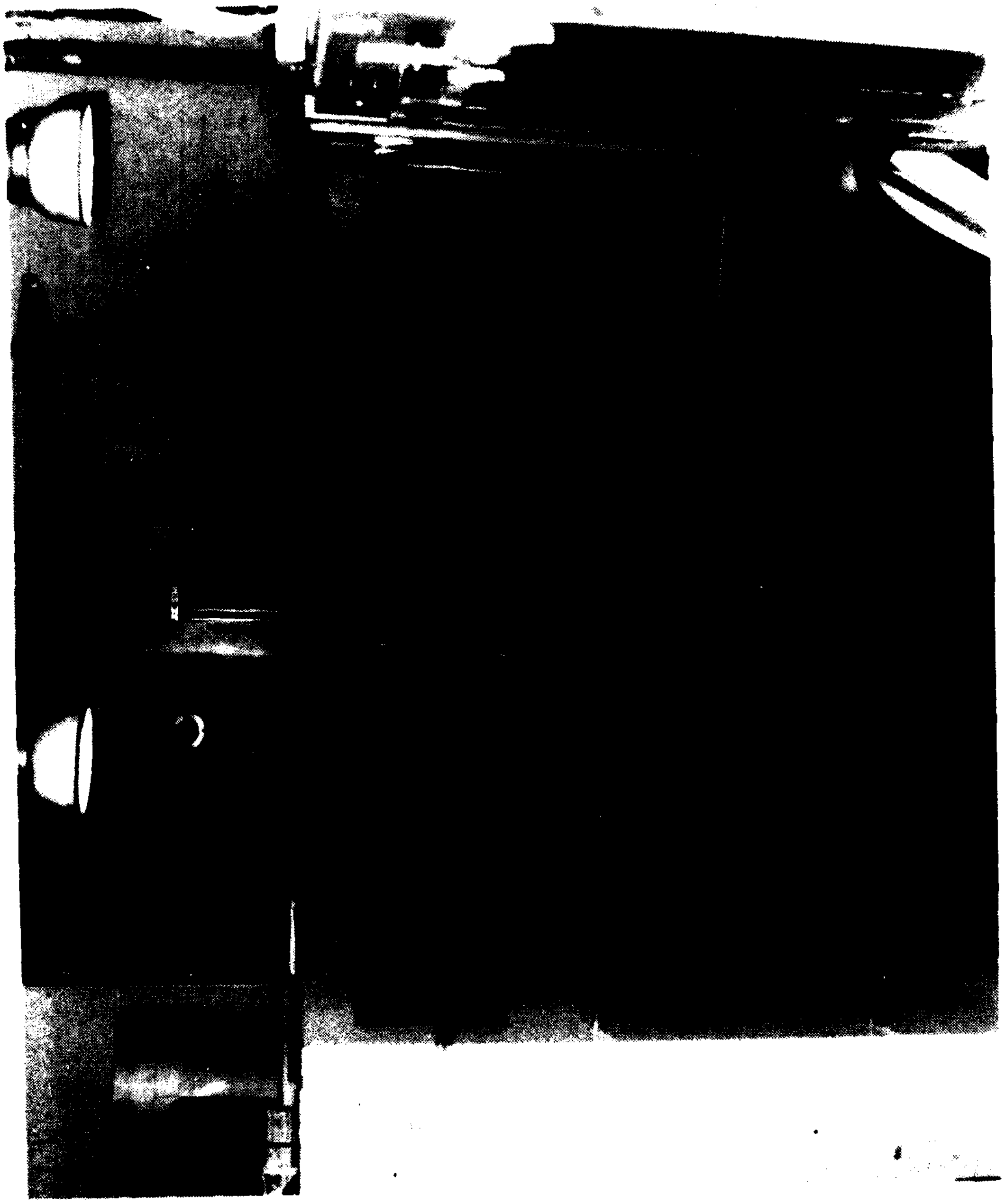

Figure 3. Storage Facilities

Figure 4. Abuse Test Facilities with the Internal Short Circuit Test Apparatus

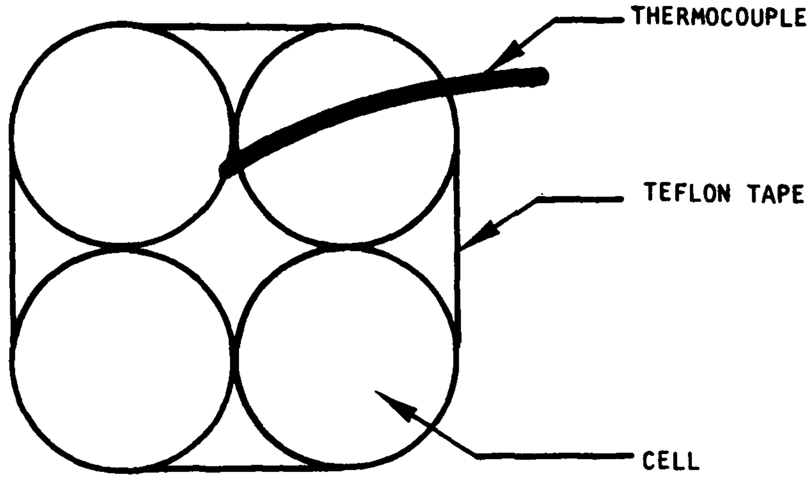

Figure 5. Thermocouple Position on Battery Pack

SECTION IV

TEST RESULTS

1. FRESH CELL PERFORMANCE TEST

The capacities of the Honeywell "0.6D" size pilot production cells were determined to a 2.0 volt end-of-discharge voltages at constant current loads of 50MA, 100MA, 200MA, and 400MA at temperatures of -65°F, -40°F, 0°F, 30°F, 70°F, 100°F, and 140°F. This test was designed to characterize the cell performance over a wide range of operational conditions. Figure 6 graphically presents cell capacities as a function of temperature at the various rates of discharge. Statistical data on this fresh cell performance test for both the first EPC and pilot production cell is presented in Appendix B to this report. These same curves are presented individually with graphic representations of capacity variation for both the first EPC and production cells and are included as Appendix B to this report.

An evaluation of the discharge rate capability of these cells at room temperature was also performed. Table 4 presents the results of this evaluation. These tests were done in a remote area. No bulging or venting occurred. Comparison of these results with the rate capability of the first EPC are made in Section V, Conclusions.

During each of the tests of capacity as a function of temperature, a measurement of the initial time for the cell to provide a minimum of 2.0 volts after the onset of a load was taken. This phenomenon is referred to as "voltage delay". This behavior was characterized during first EPC testing and was found to be unacceptable for Aircrew Life Support Equipment Application. During pilot production testing the data obtained for the 400MA discharge at -65°F was the only test exhibiting any significant voltage delay. Under conditions of 400MA discharge at -65°F, the cells exhibited approximately 6.0 seconds of this "voltage delay" phenomenon. Figure 7 is a computer print out of this test and is included to demonstrate the significance of this phenomenon. A discussion of the impact of this data is provided in Section V of this report.

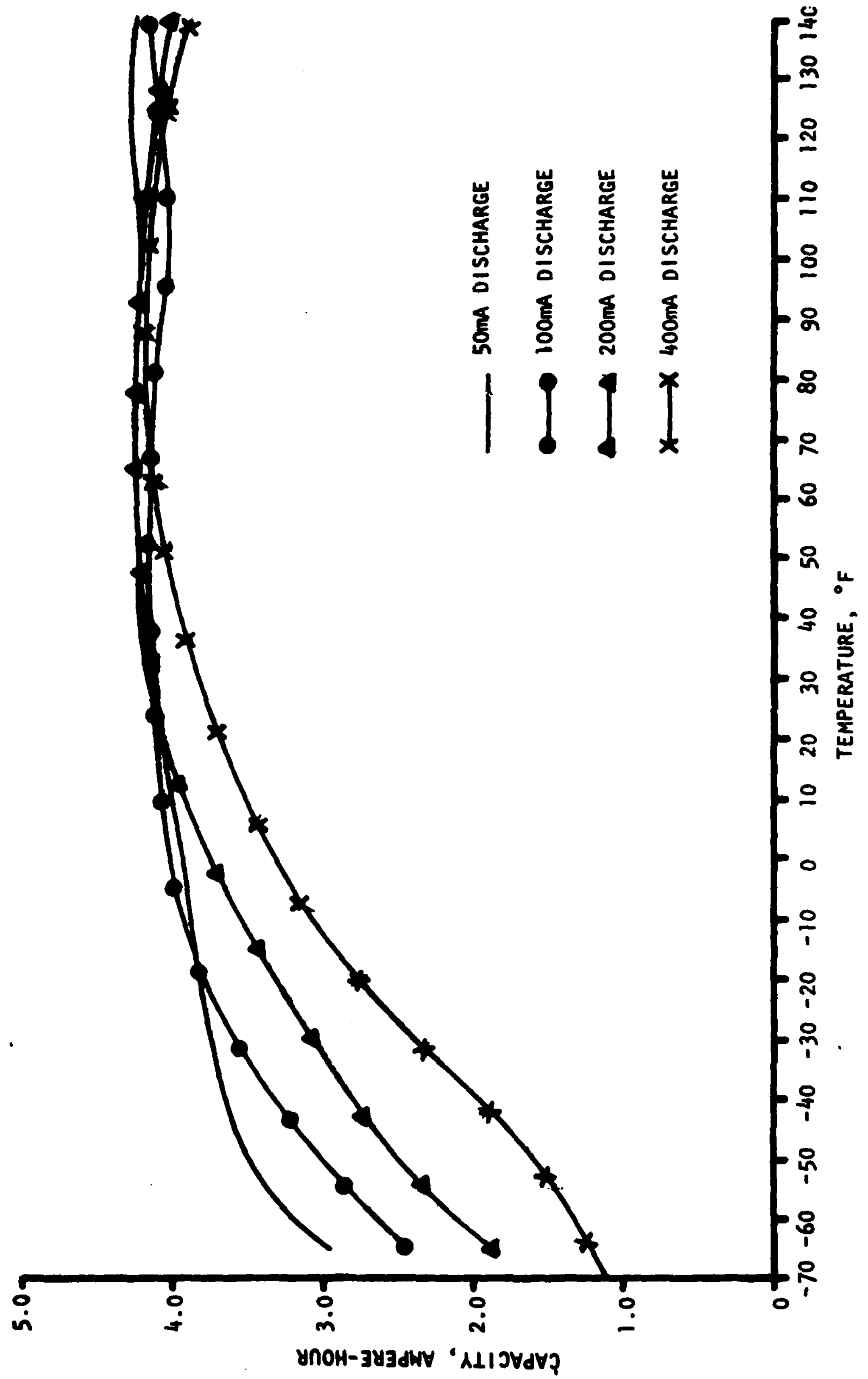

Figure 6. Cell Capacity vs. Temperature at Various Rates

TABLE 4

SUMMARY OF HIGH RATE DISCHARGE TESTING

CURRENT (AMPS)	CURRENT DENSITY (MA/CM^2)	MAX. TEMP (°C)	CAPACITY TO 2.0 VOLTS (AH)
1.00	3.47	23°C	4.12
1.50	5.21	28°C	3.85
2.00	6.94	32°C	2.83
2.50	8.68	32°C	2.95
3.00	10.42	39°C	2.68
3.50	12.15	39°C	2.16
4.00	13.88	42°C	2.22
5.00	17.36	49°C	1.80

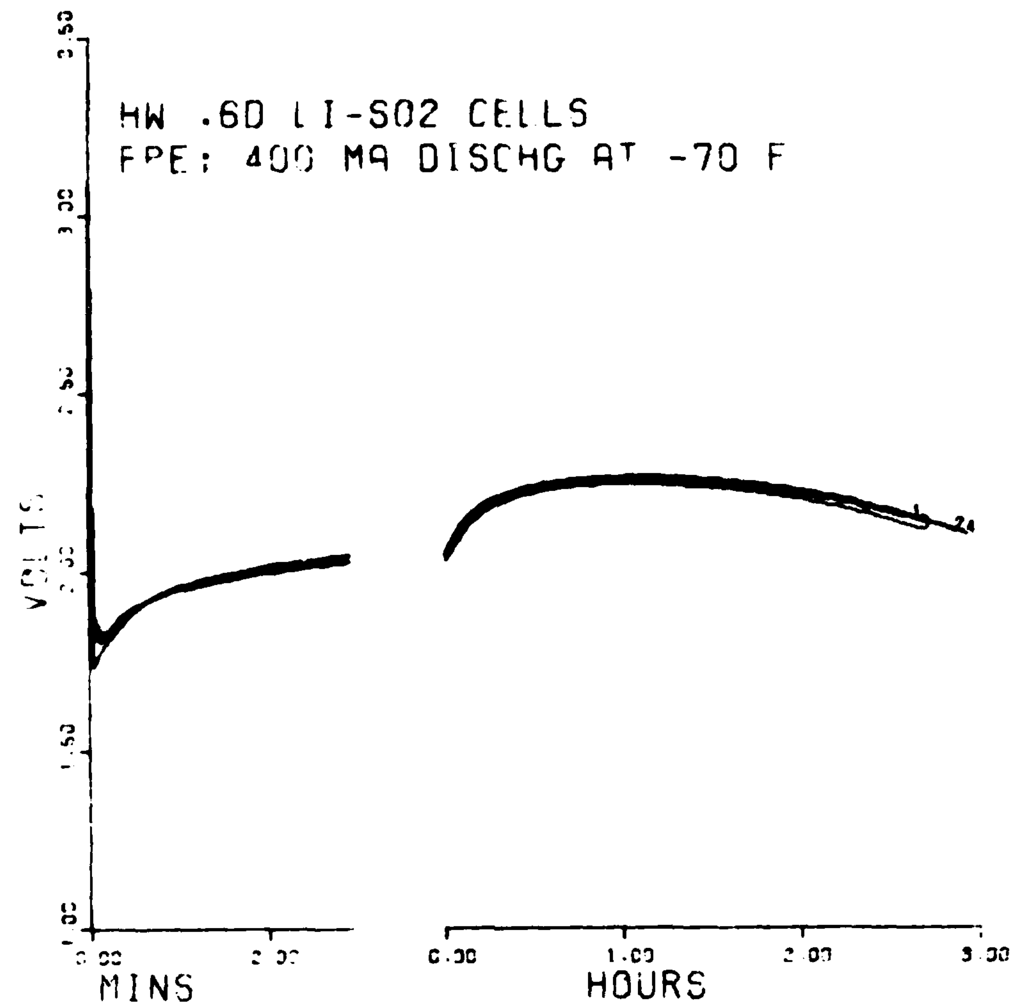

Figure 7. 400MA Discharge at -70°F Showing Voltage Delay

2. ABUSE TESTING

Abuse testing was accomplished according to the test matrix provided in Section IV of this report. All testing was performed at a remote test site with adequate protection and ventilation provided for personnel.

External short circuit tests were performed on cells and batteries at room temperature at at -40°F. Figures 8 and 9 are graphs of the cell current, voltage, and temperature under external short circuit conditions at room temperature and -40°F respectively. It can be seen that reduction in test temperature produces two effects. Cells externally short circuited at room temperature vented at approximately 1.8 minutes with a cell skin temperature of 57°C (135°F). Cells externally short circuited after being soaked at -40°F vented at approximately 3.0 minutes with a cell skin temperature of 22°C. In both cases, cells vented mildly through the vent mechanism with no flame present. Figure 10 is a visual comparison of an intact cell versus a vented cell after application of an external short circuit.

Four cell series connected batteries were also externally short circuited with one battery stabilized initially at room temperature and one battery soaked at -40°F for approximately 12 hours prior to application of the short circuit type load. Figures 11 and 12 are included to graphically present the electrical behavior of these batteries under short circuit conditions at room temperature and -40°F respectively. It can be seen from the data that during short circuit conditions at both temperatures two cells vented before battery current dropped to a minimum value. As in the single cell short circuit test. A test temperature reduction to -40°F caused only the effect of delaying the venting action. Differences were noted between cell and battery short circuit testing. In the battery configuration the cell skin temperature observed at venting was higher than seen during single cell short circuit testing. Maximum temperature attained during battery short circuit testing was also higher than observed during single cell testing. In cell level short circuiting a temperature of 57°C was reached at venting followed by an immediate decrease in temperature. During battery level short circuit testing cells were observed to vent mildly at temperatures between 65°C and 70°C. A maximum battery

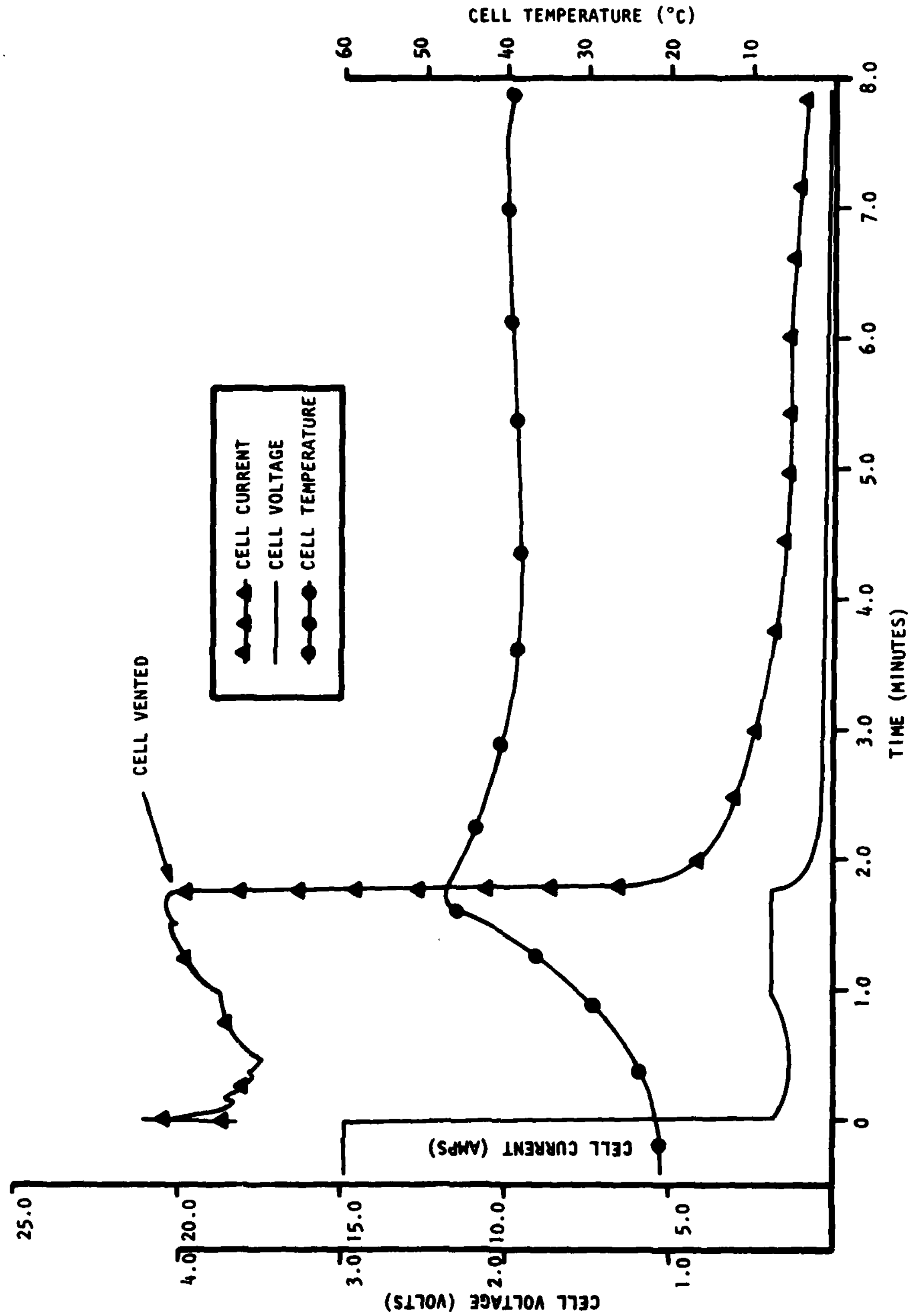

Figure 8. Cell External Short Circuit Test at Room Temperature

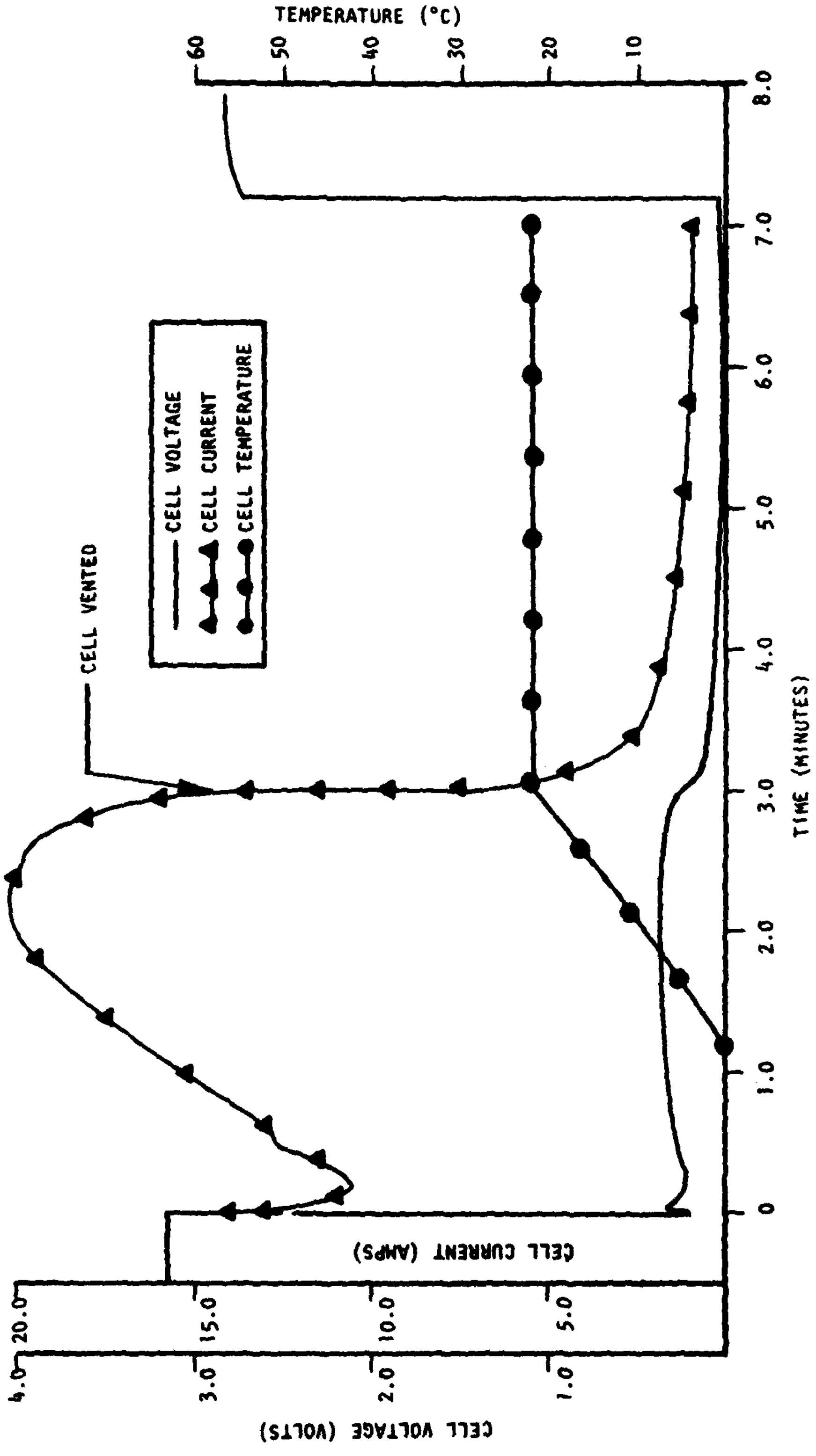

Figure 9. Cell External Short Circuit Test at -40°F

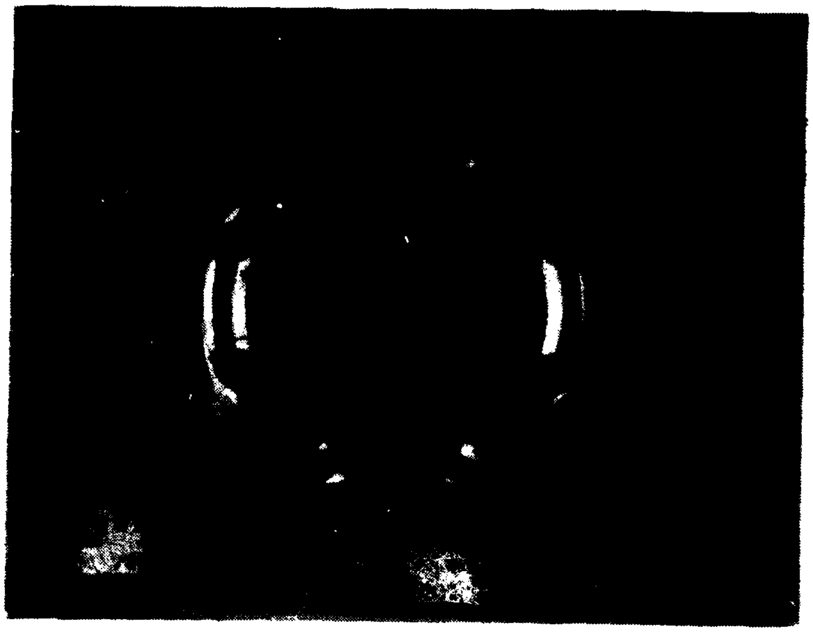

Figure 10. Comparative Photos of Intact vs. Vented Cell

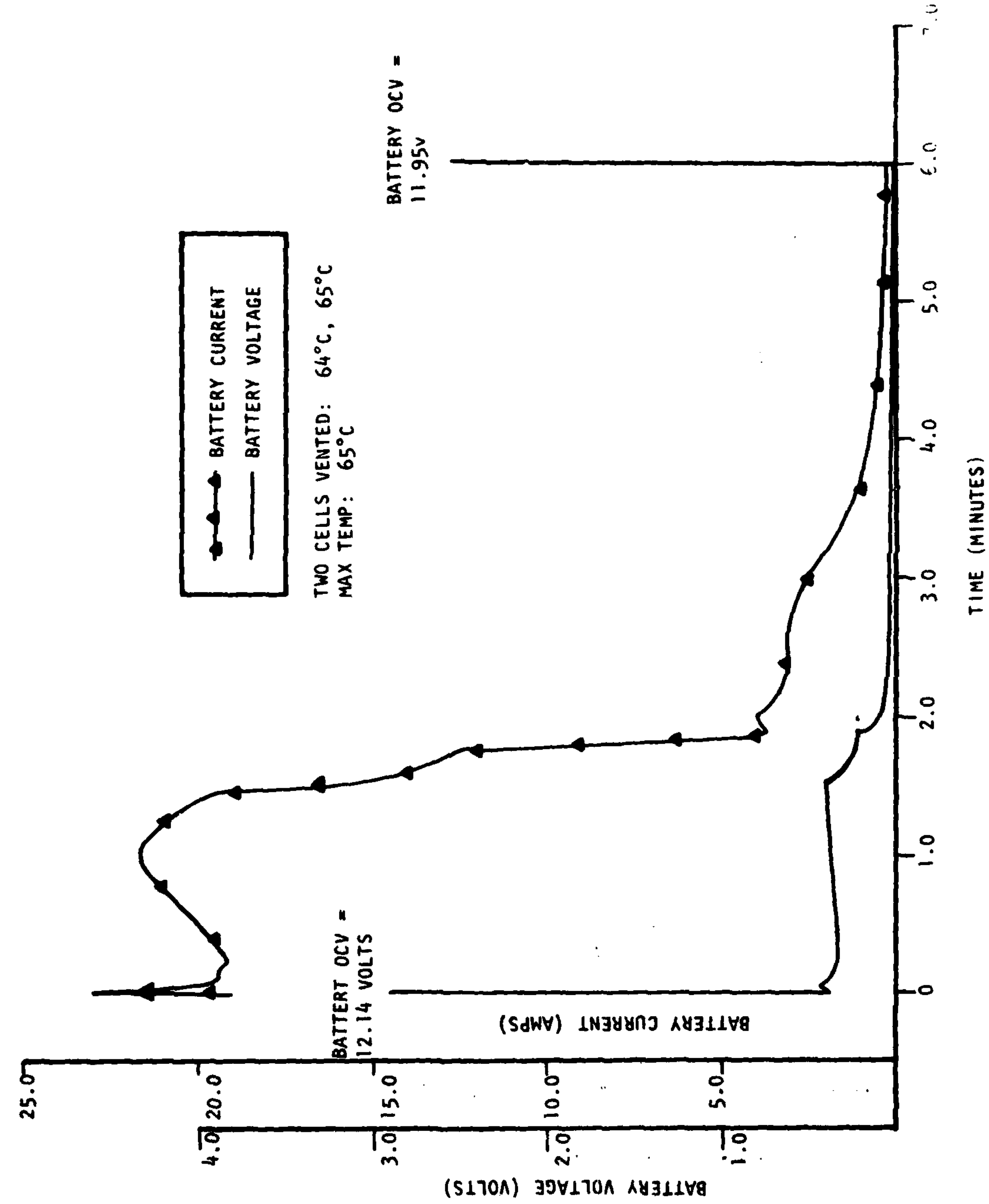

Figure 11. Battery External Short Circuit Test at Room Temperature

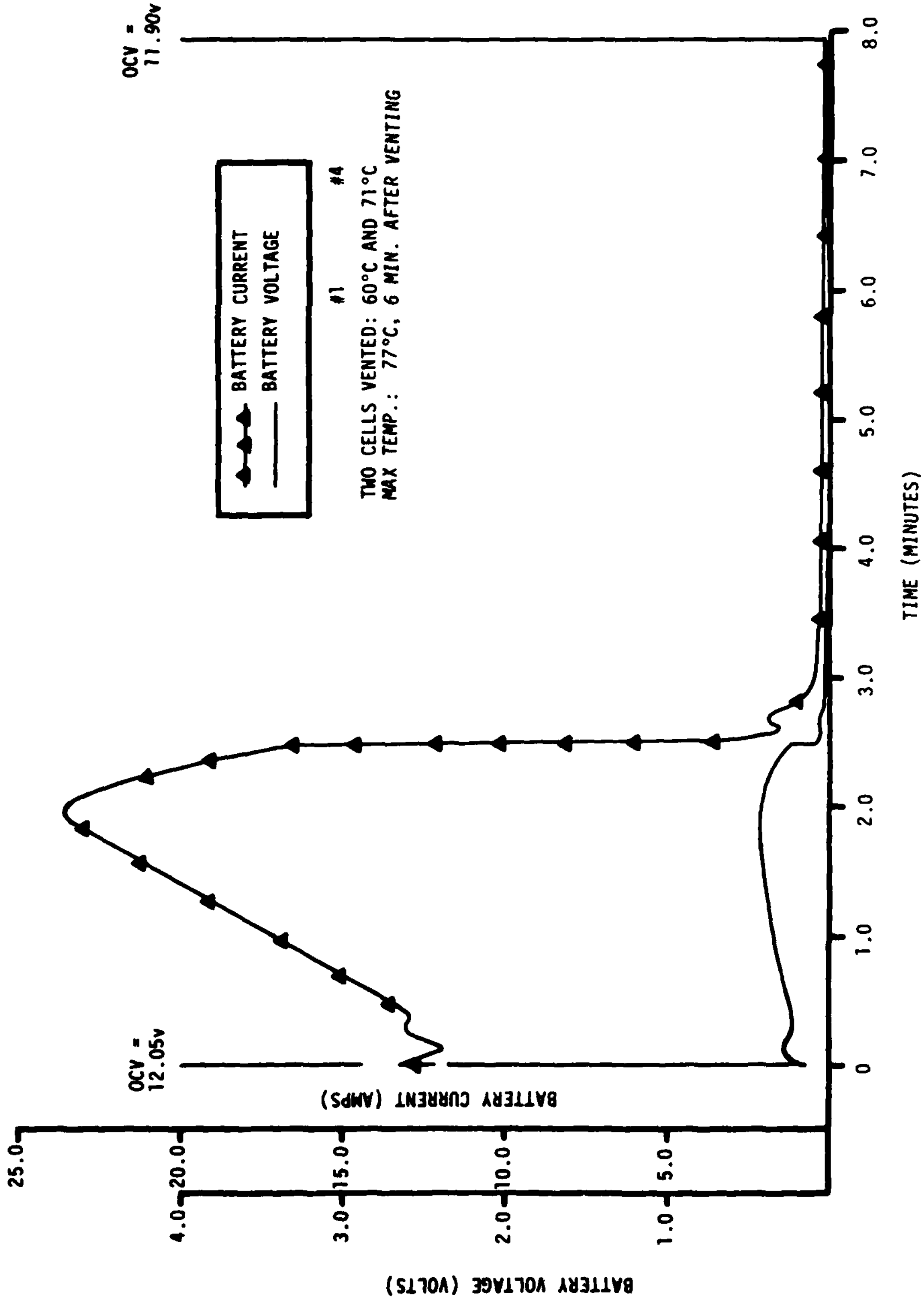

Figure 12. Battery External Short Circuit Test at -40°F

temperature of 77°C was observed 6.0 minutes after venting under conditions of -40°F. Figure 13 is included to show the venting action of the cells when constructed as a battery.

An internal short test was performed on cells at room temperature and at -40°F. Internal short circuiting was accomplished through the use of nail penetration through the cell case and the nail was left intact within the cell after penetration. A hydraulic fixture was constructed which delivered the nail through the cell in the direction perpendicular to the cell wrap. This orientation provided for a maximum abusive conditions in that the nail would penetrate the lithium anode numerous times and guarantee a complete internal short circuit. Figure 14 shows the operation of this hydraulic device. The behavior of the cells under this internal short circuit condition at room temperature at at -40°F is shown in Figures 15 and 16 respectively. In both cases cells did not vent. Maximum temperatures reached after penetration were both below 30°C and a difference of only a few degrees in temperature was observed between the tests at room temperature and -40°F. Within 15 minutes both test cells had returned to approximately 20°C. It was noted that during the -40PF test the internal short circuit was momentarily lost. The nail was not removed from the cell throughout the test. This phenomenon may have occurred from the rapid growth of a film on the nail or on the lithium. This film may have been, for a short time, capable of allowing the cell to seek an open circuit voltage. The behavior of the cells under nail penetration was relatively benign with no rapid heat generation or venting. Sulfur dioxide and the electrolyte slowly leaked from the cells and no other reactions were observed. Figure 17 presents photographs of a cell that has been penetrated by the nail. The corrosion had been developed after electrolyte exposure for several days.

Forced overdischarge tests were performed on cells at both room temperature and at -40°F. Three rates of discharge/overdischarge were tested at each temperature. Figures 18, 19, and 20 show the behavior of cells under room temperature forced overdischarge conditions at 300MA, 1000MA, and 2000MA respectively. Figures 21, 22, and 23 show cell behavior under

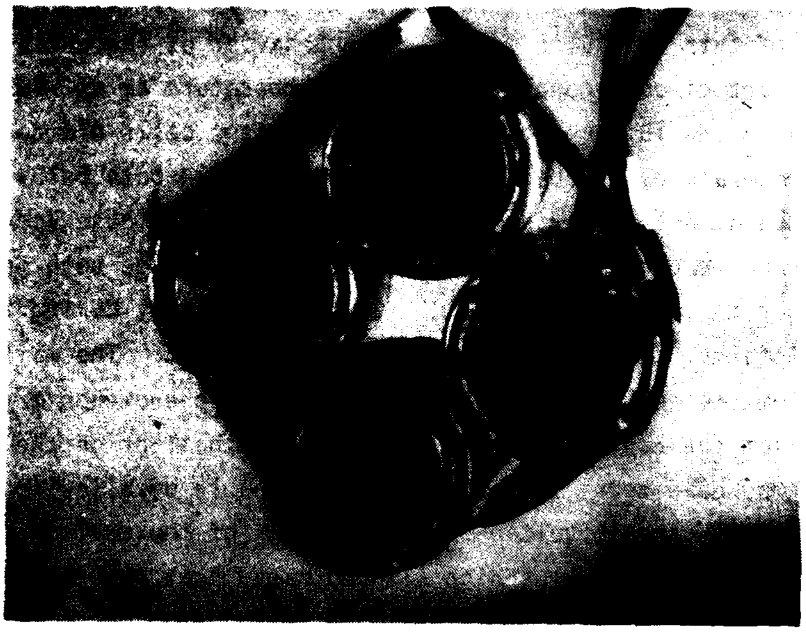

Figure 13. Photo of Battery Pack after Short Circuit Testing

Figure 14. Operation of Internal Short Circuit Device

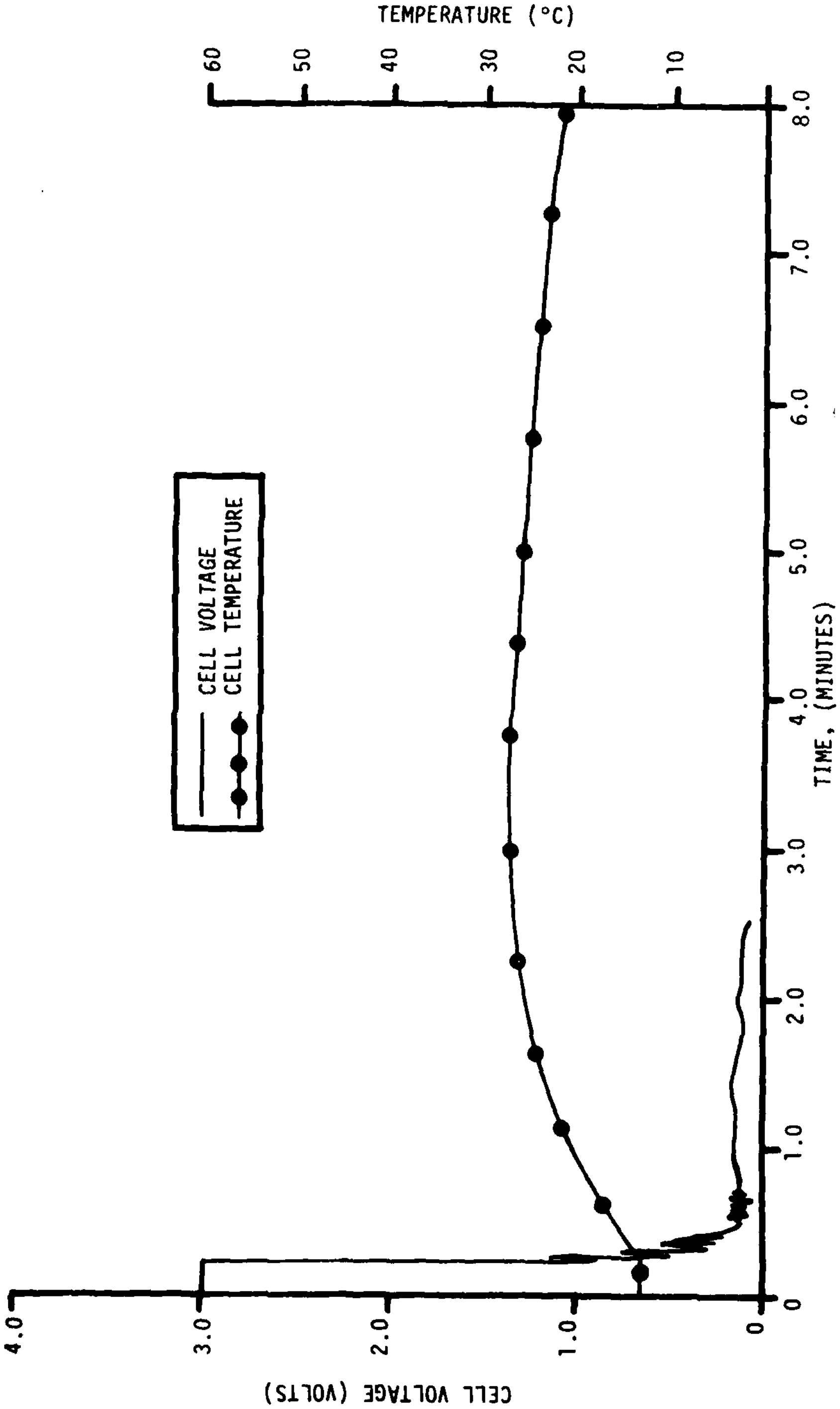

Figure 15. Cell Puncture Test at Room Temperature

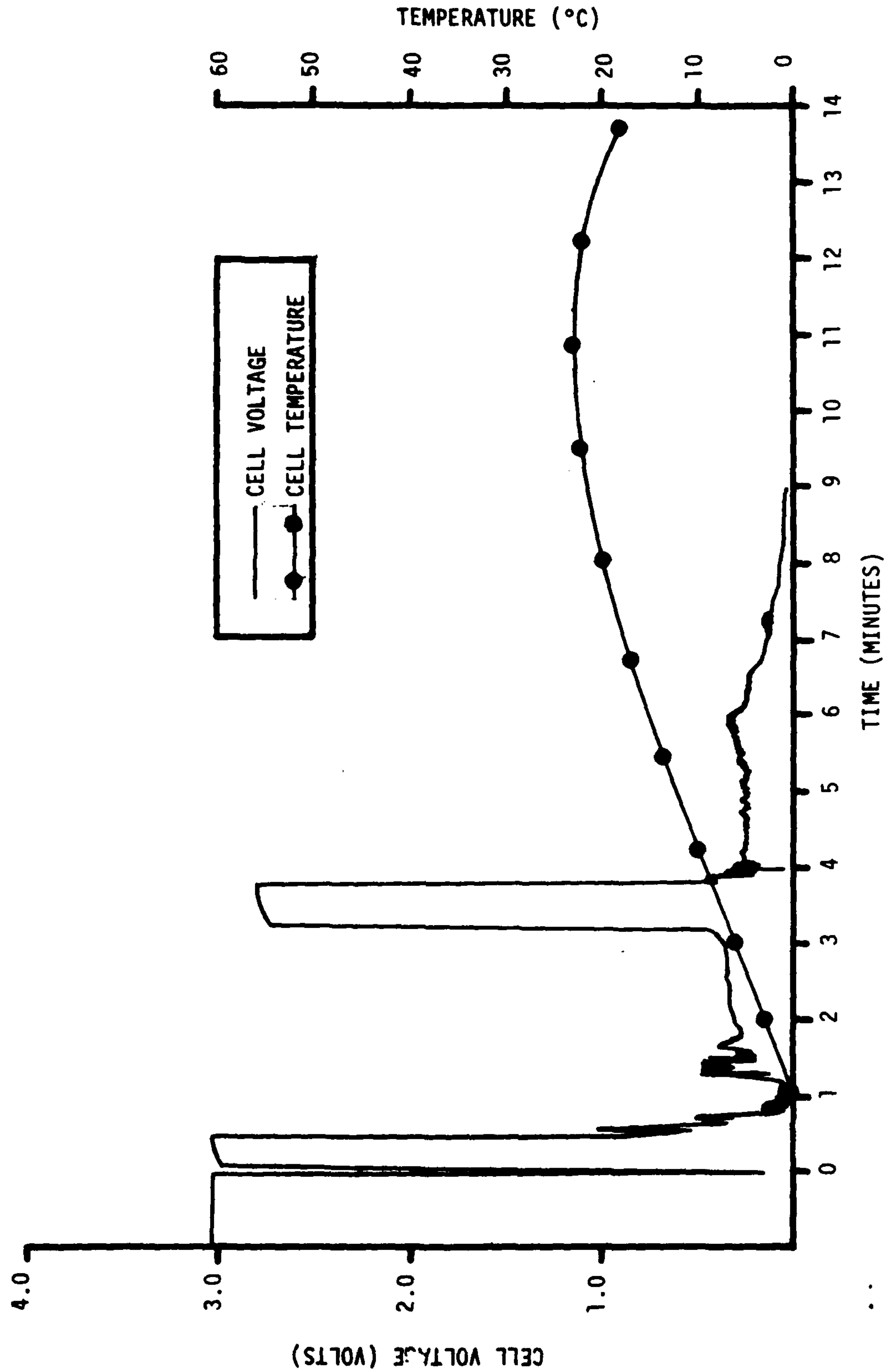

Figure 16. Cell Puncture Test at -40°F

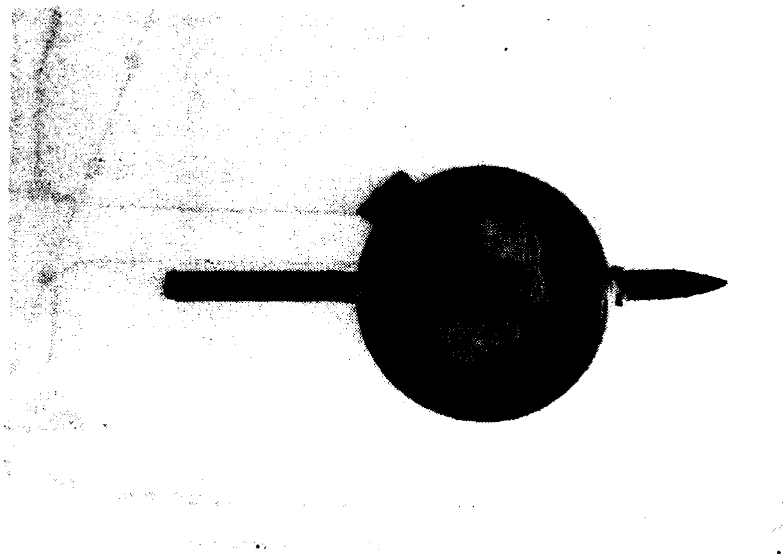

Figure 17. Nail Penetrated Cell - Side View

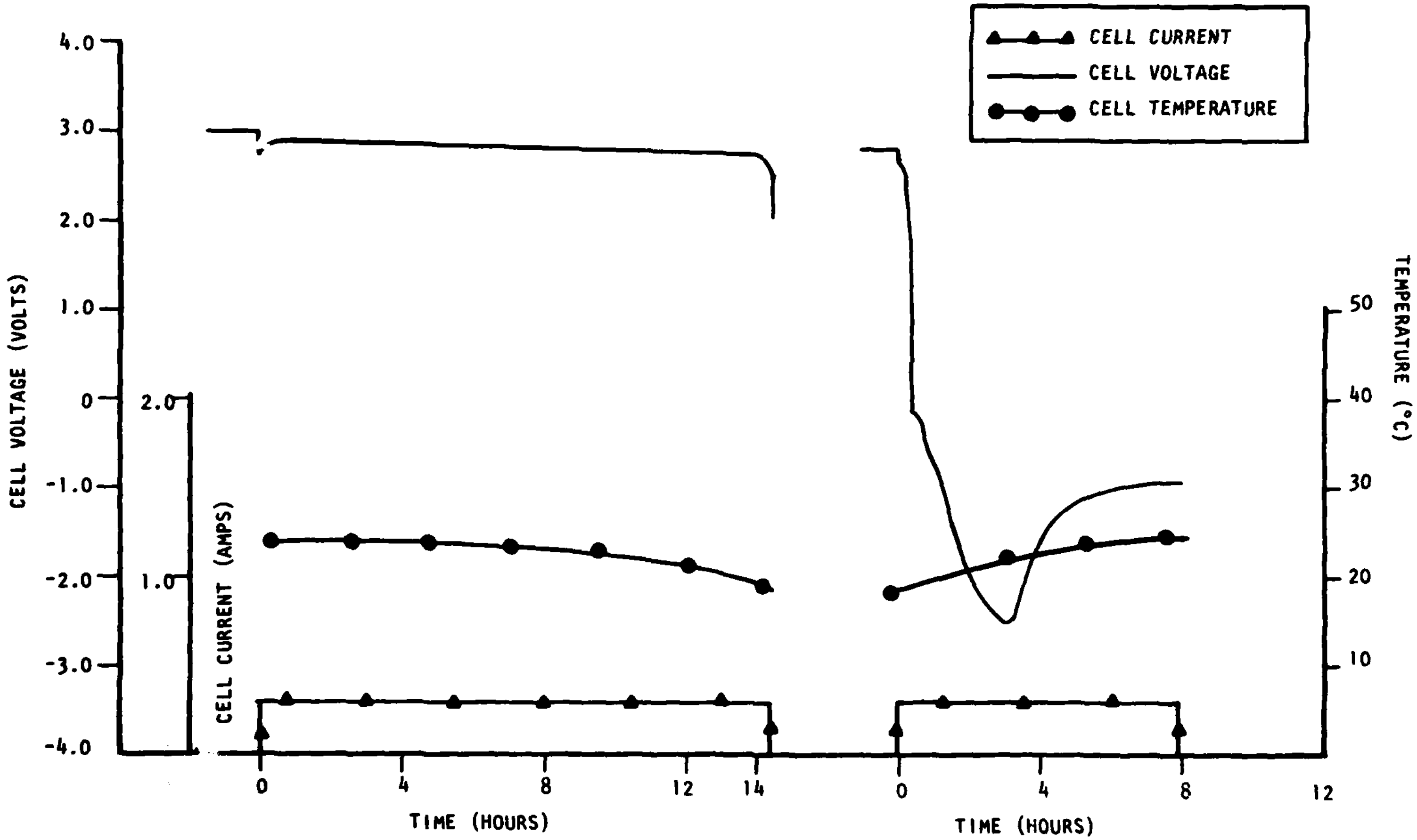

Figure 18. Forced Overdischarge Test at 300MA Constant Current at Rocm Temperature

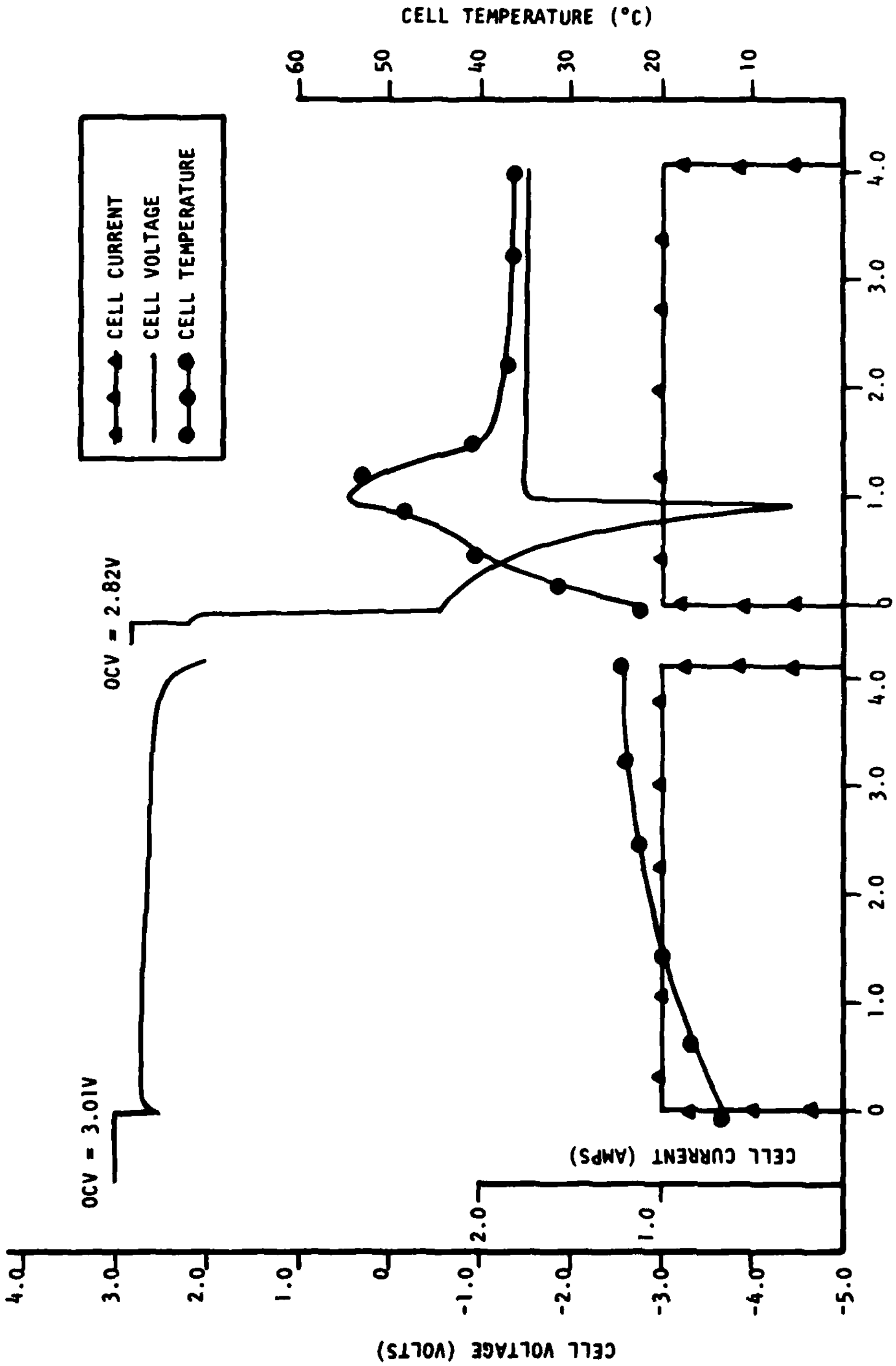

Figure 19. Forced Overdischarge Test at 1.0 Ampere Constant Current at Room Temperature

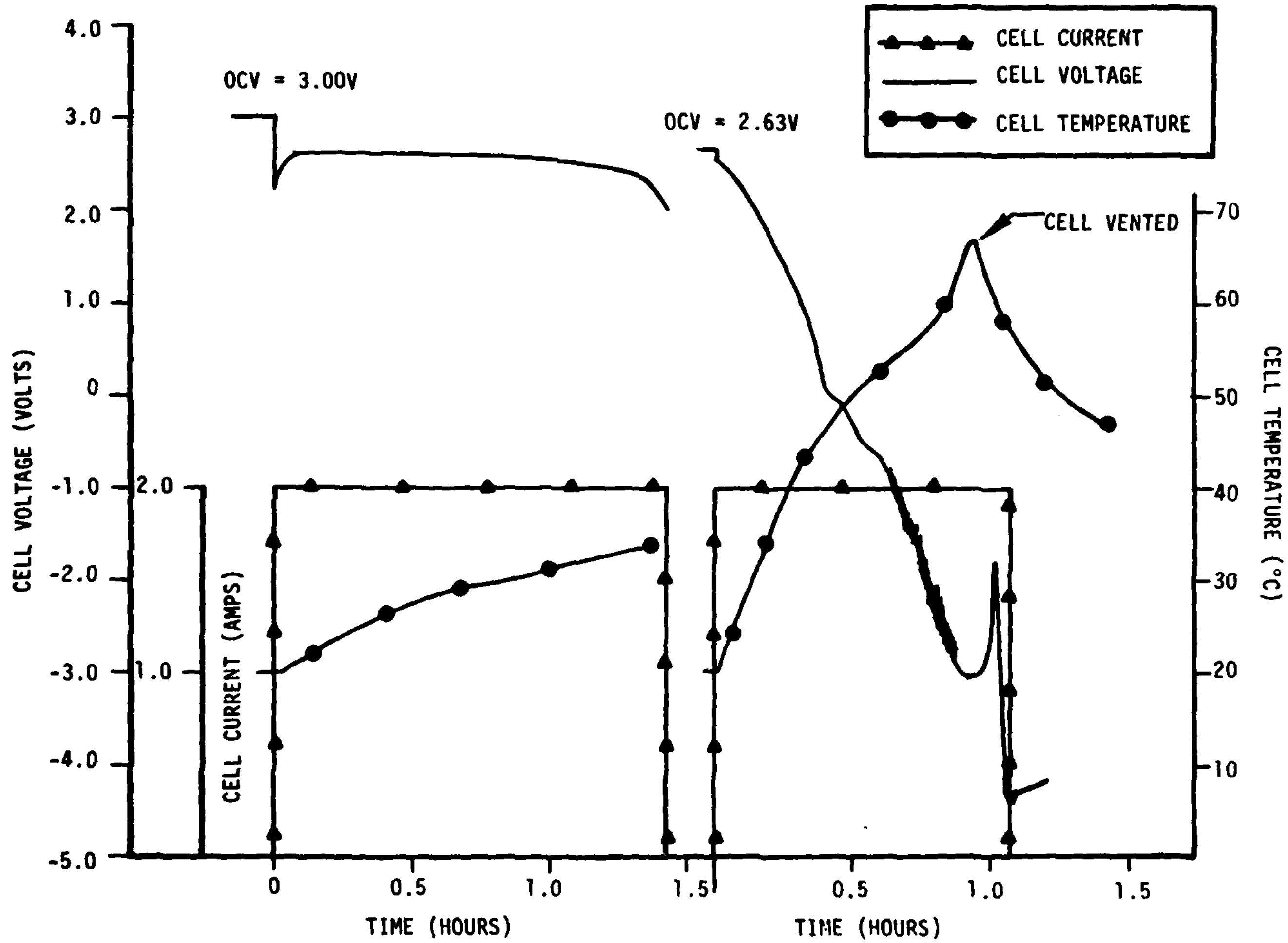

Figure 20. Forced Overdischarge Test at 2.0 Ampere Constant Current at Room Temperature

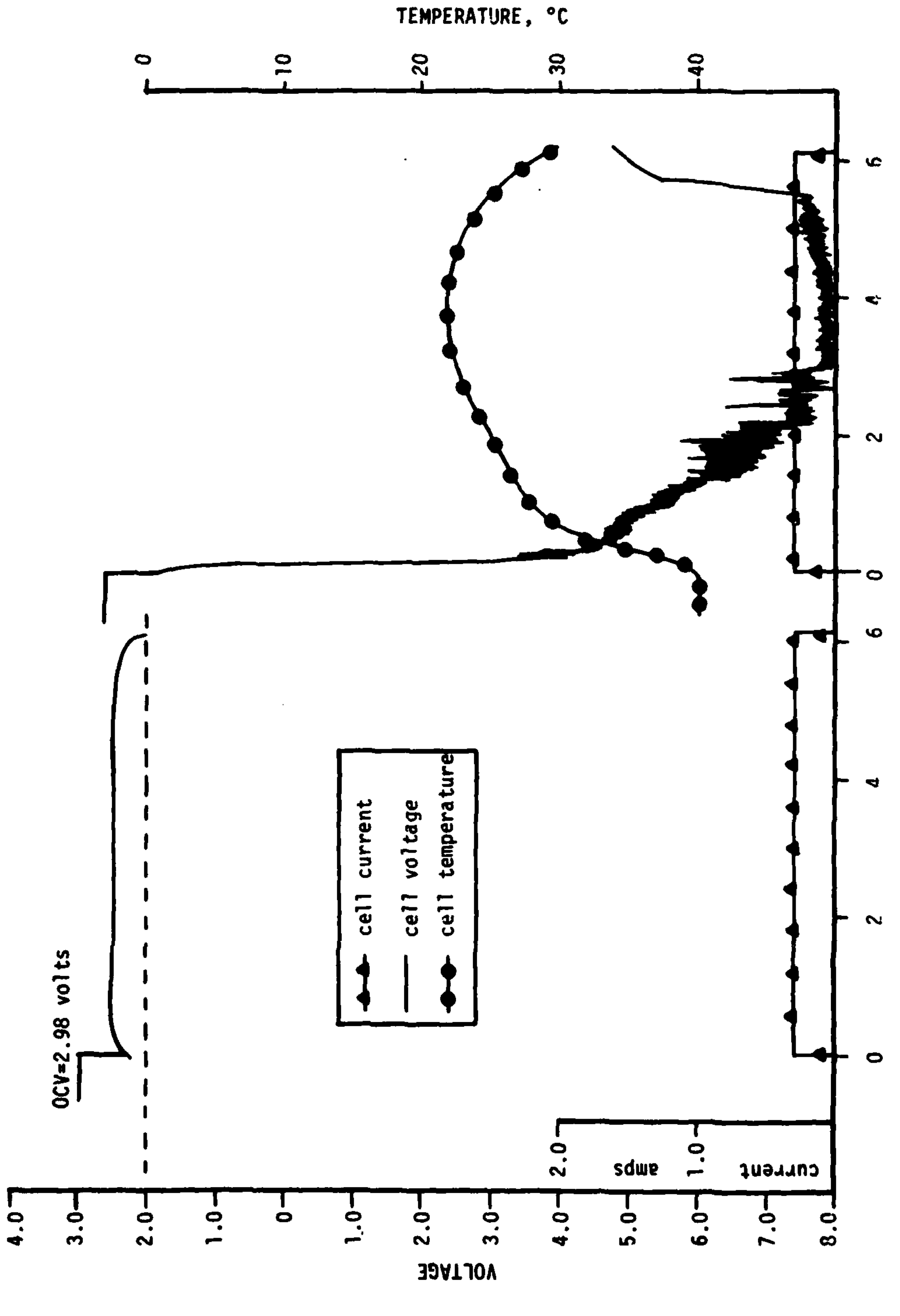

Figure 21. Force Overdischarge Test at 300 MA Constant Current Rate at -40°C

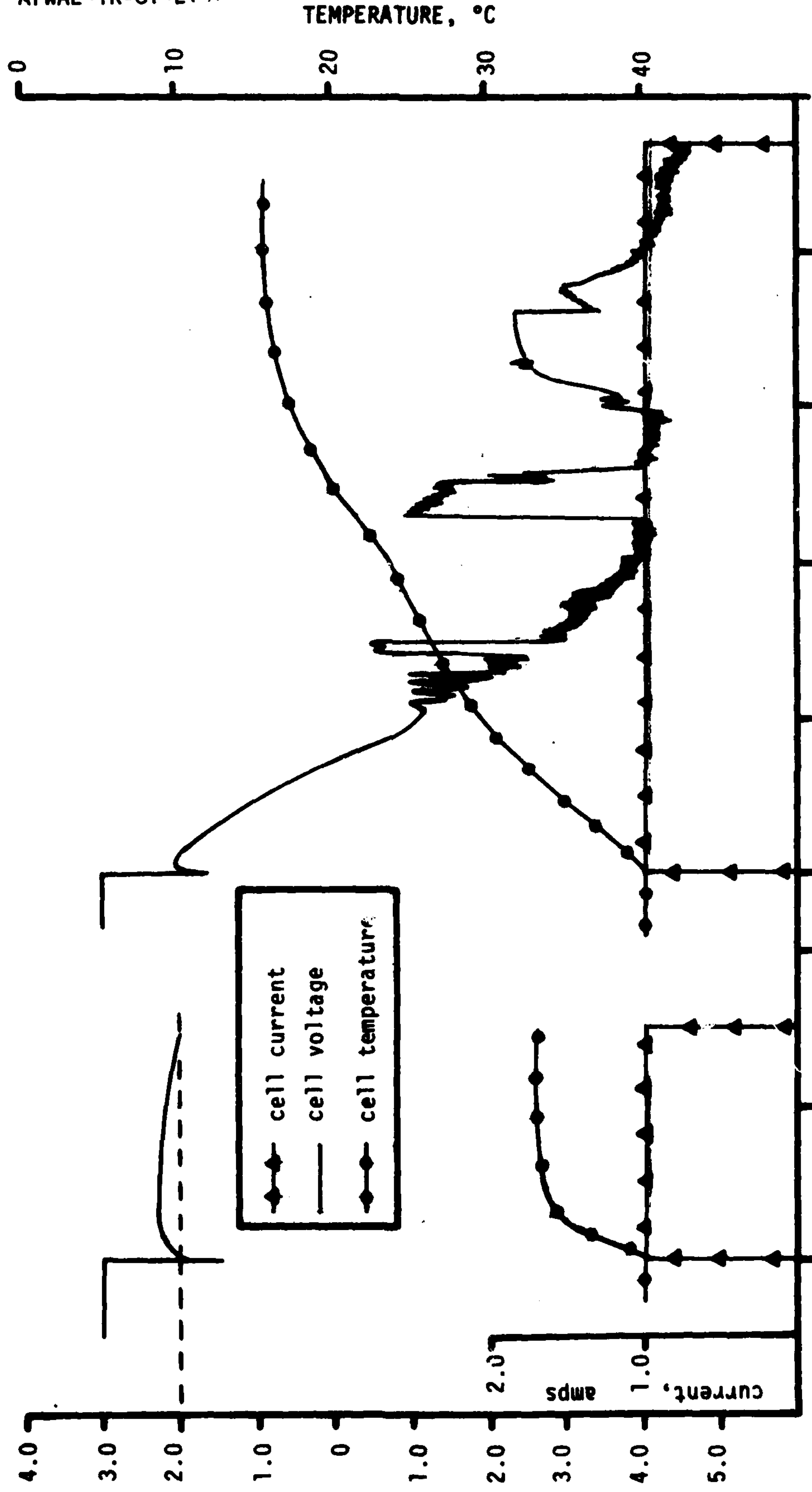

Figure 22. Forced Overdischarge Test at 1.0 Ampere Constant Current Rate at -40°C

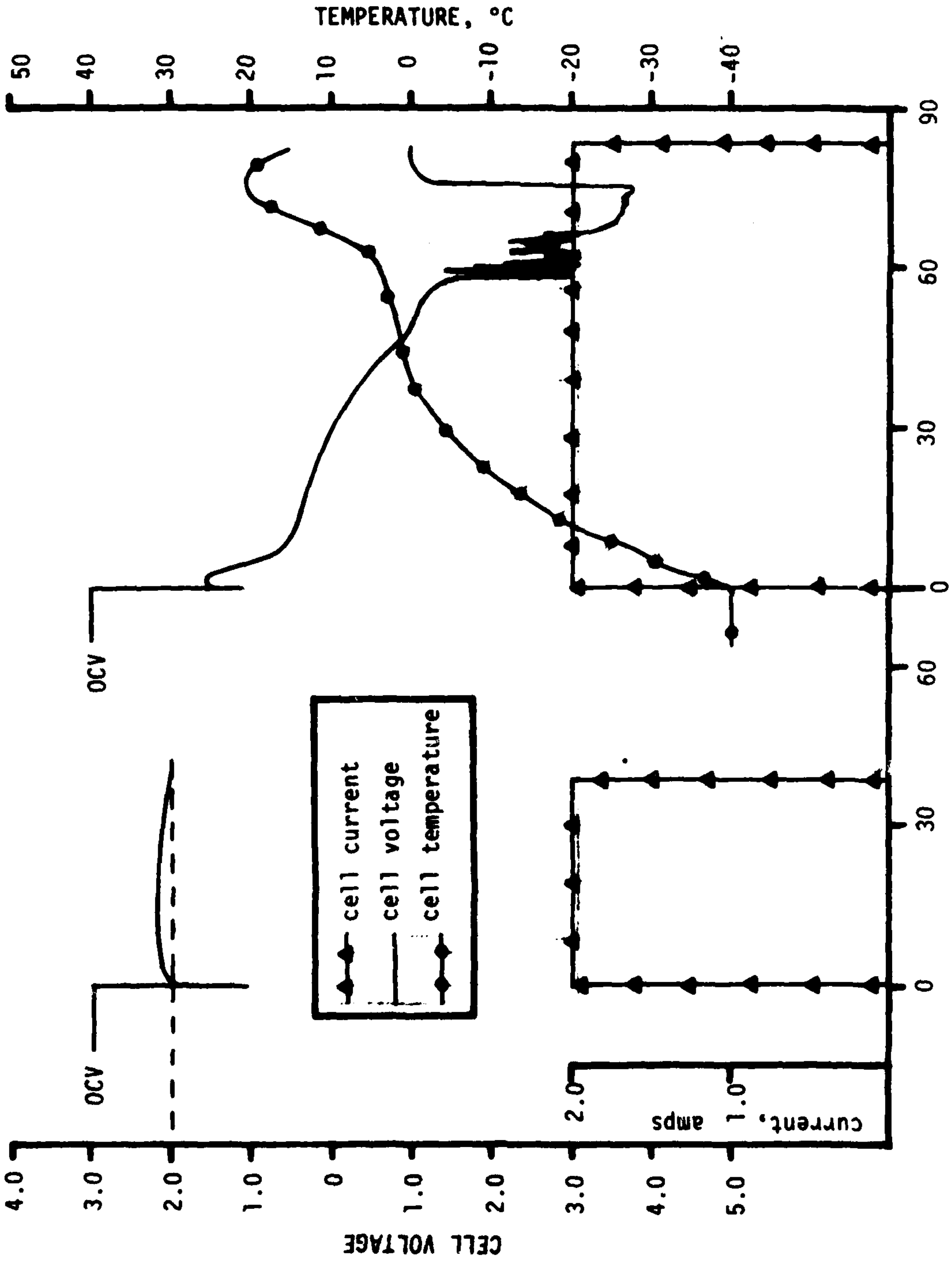

Figure 23. Forced Overdischarge Test at 2.0 Ampere Constant Current Rate at -40°C

analogous tests at -40°F. Table 5 is included as a summary of the forced overdischarge test data. From the data, several generalizations can be made.

It was observed that the rate of current being forced into the cell after discharge to the 2.0 volt cut-off at room temperature correlates positively with the maximum temperature observed at the cell case. The maximum temperature measured was +65°C during the 2.0 ampere reversal. Flame venting was observed only during the 2.0 ampere reversal. The shapes of the temperature curves of the 1.0 ampere and 2.0 ampere curves (Figures 19 and 20) are similar whereas in Figure 18 no discernible temperature peak was observed.

Voltage noise present in the overdischarge region of the voltage curves for the -40°C tests was greater than observed in the analogous room temperature tests. Increasing the rate of forced overdischarge at either temperature caused voltage fluctuations to become more pronounced. In some tests, the forced overdischarge test condition was maintained for greater than 100% of cell capacity above 2.0 volts. This was done to allow for stabilization of cell temperature. In all cases, it can be seen that the slope of the temperature curve increased more rapidly during the onset of rapid voltage fluctuation or the plunging of the voltage curve to greater negative voltage.

3. STORAGE TESTING

An evaluation of the cells' capability to retain electrical capacity with time was performed at temperature of 160°F (high temperature), room temperature, and 32°F (cold temperature). All cells were stored in an upright position. All cells were discharged at the prescribed time of storage under a 300MA constant current load to a 2.0 volt end-of-discharge voltage.

TABLE 5

SUMMARY FORCED OVERDISCHARGE TESTING

TEST (°C) TEMPERATURE	CURRENT (AMPS)	CURRENT DENSITY	CAPACITY TO 2.0 VOLTS	OPERATING VOLTAGE	MAX TEMP OBSERVED (°C)	REMARKS
25°C	0.30	$1.04 MA/CM^2$	4.27AH	2.8	24	NO REACTION
25°C	1.0	$3.47 MA/CM^2$	4.10AH	2.7	54	NO REACTION
25°C	2.0	$6.94 MA/CM^2$	2.83AH	2.5-2.6	67	VENTING/ SLIGHT FLAME
-40°C	0.30	$1.04 MA/CM^2$	1.83AH	2.5	-22	NO REACTION
-40°C	1.0	$3.47 MA/CM^2$	1.49AH	2.2-2.3	-16	NO REACTION
-40°C	2.0	$6.9 MA/CM^2$	1.30AH	2.1	-19	NO REACTION

The results of the high temperature storage test are shown in Figure 24. The propeller shape of the data points is given to provide some indication of variation of individual cell capacities. The dot in the circle represents the arithmetic mean and the top and bottom of the propeller shape represents ±1 standard deviation from the mean. The upper set of data points represents cell discharge at room temperature while the lower set of data represents cell discharge at -40°F. No cells vented nor was SO_2 leakage detected during the nine months of testing. The computer printouts for the discharge of the high temperature storage cells at 70°F and -40°F is included in this report as Appendix C.

The results of the room temperature storage test are shown in Figure 25. It should be noted that two data points are shown for the two year (24 months) storage data point. The lower value point with the large standard deviation represents the discharge of six cells incorporating Honeywell's standard glass-to-metal seal as of the time these cells were manufactured. The higher value data point is representative of the discharge of six cells incorporating a new glass-to-metal seal which became available while the pilot production cells were being fabricated. These "new seal" cells were manufactured in the same lot as the pilot production cells and have been stored under the identical conditions as cells in this test. Data shown for nine months at room temperature is unexplainable since no postmortem analyses have been performed and subsequent data is more indicative of fresh cell performance. It should also be noted that both room temperature and low temperature storage evaluations are still on-going. A sufficient quantity of cells to provide data for five years has been stored in each condition.

Figure 26 represents the data obtained thus far in the low temperature storage evaluation. Within experimental error, no loss in capacity has yet been realized.

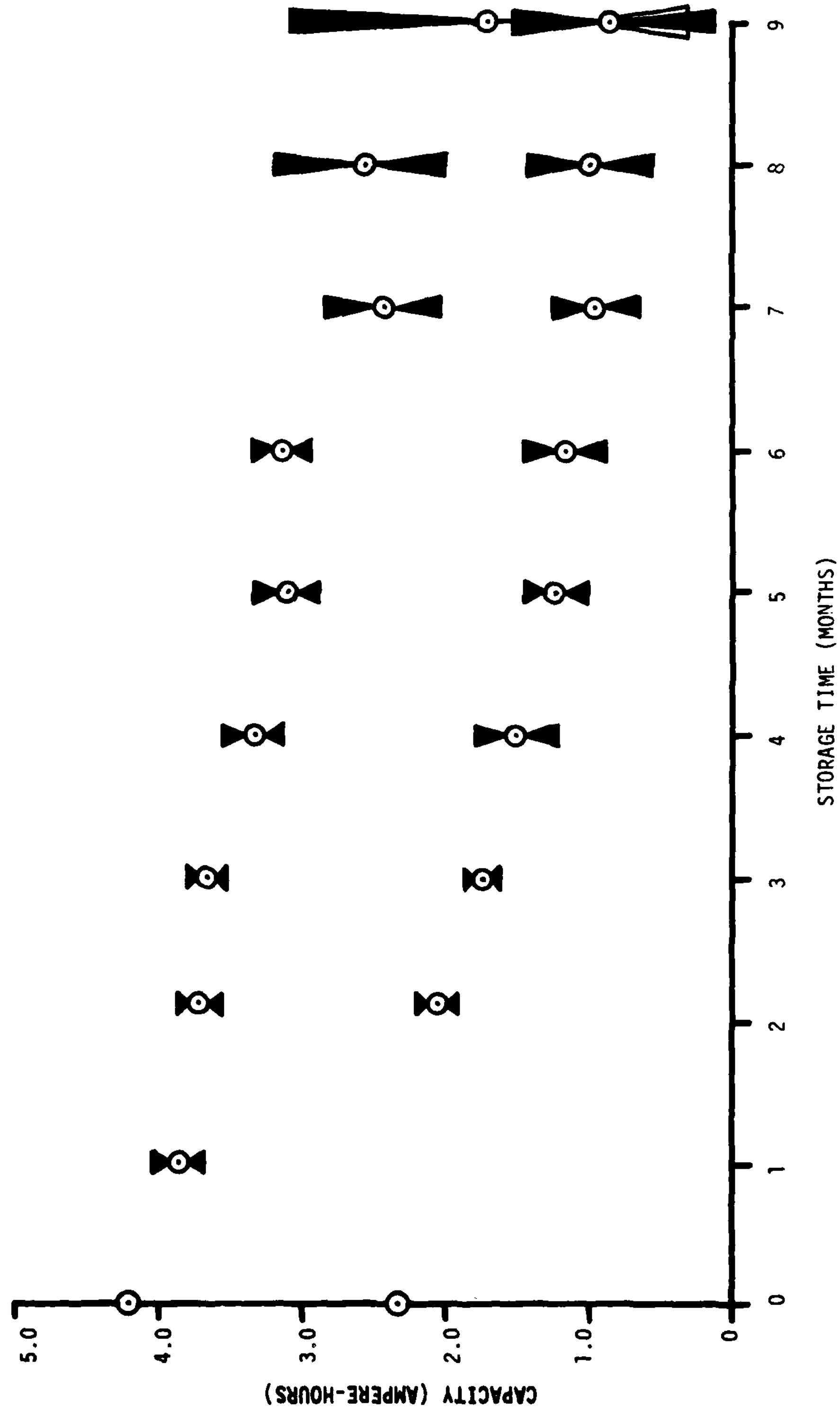

Figure 24. Capacity at Room Temperature and -40°F vs. Storage Time at Elevated Temperature

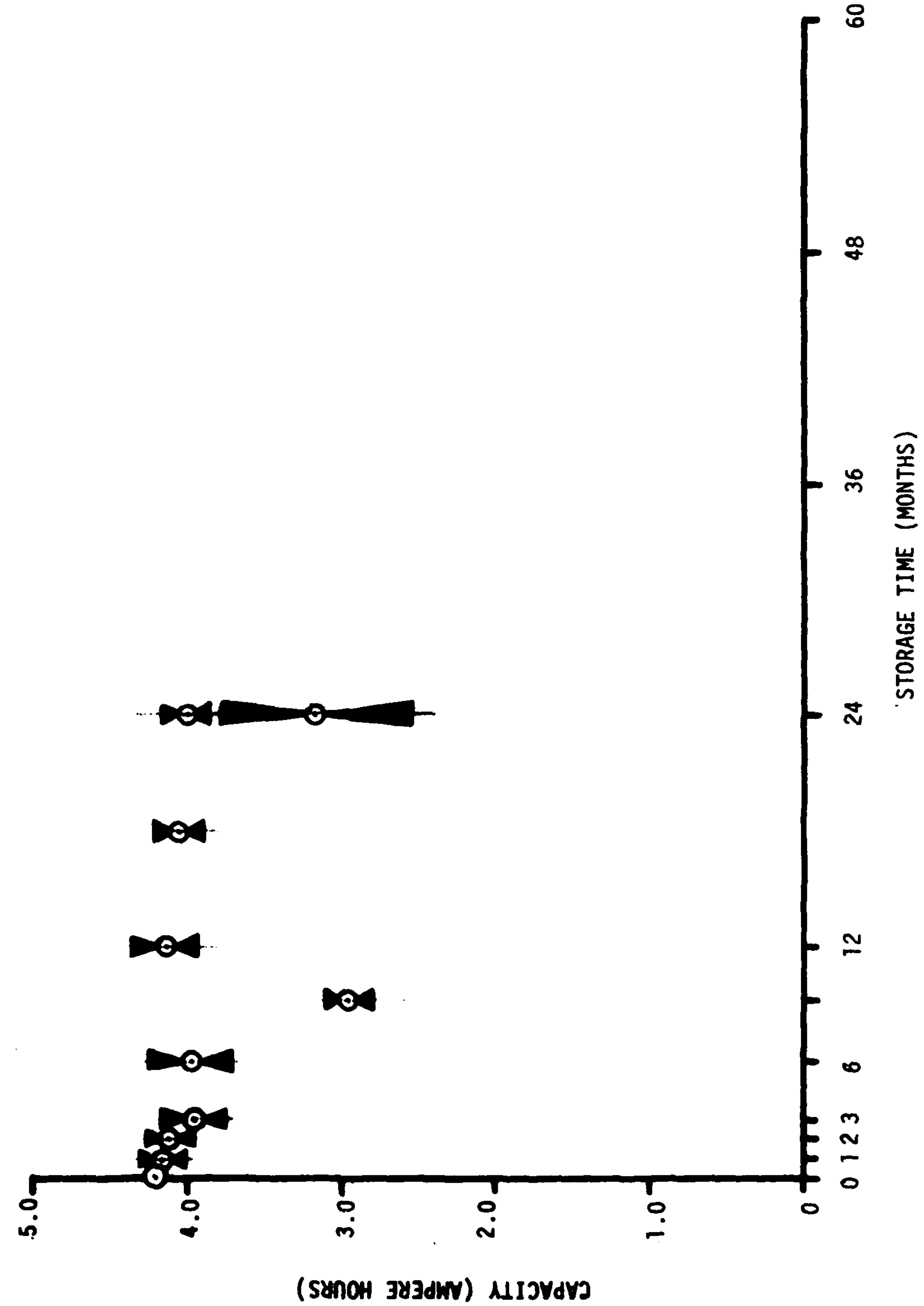

Figure 25. Capacity vs. Storage Time at Room Temperature

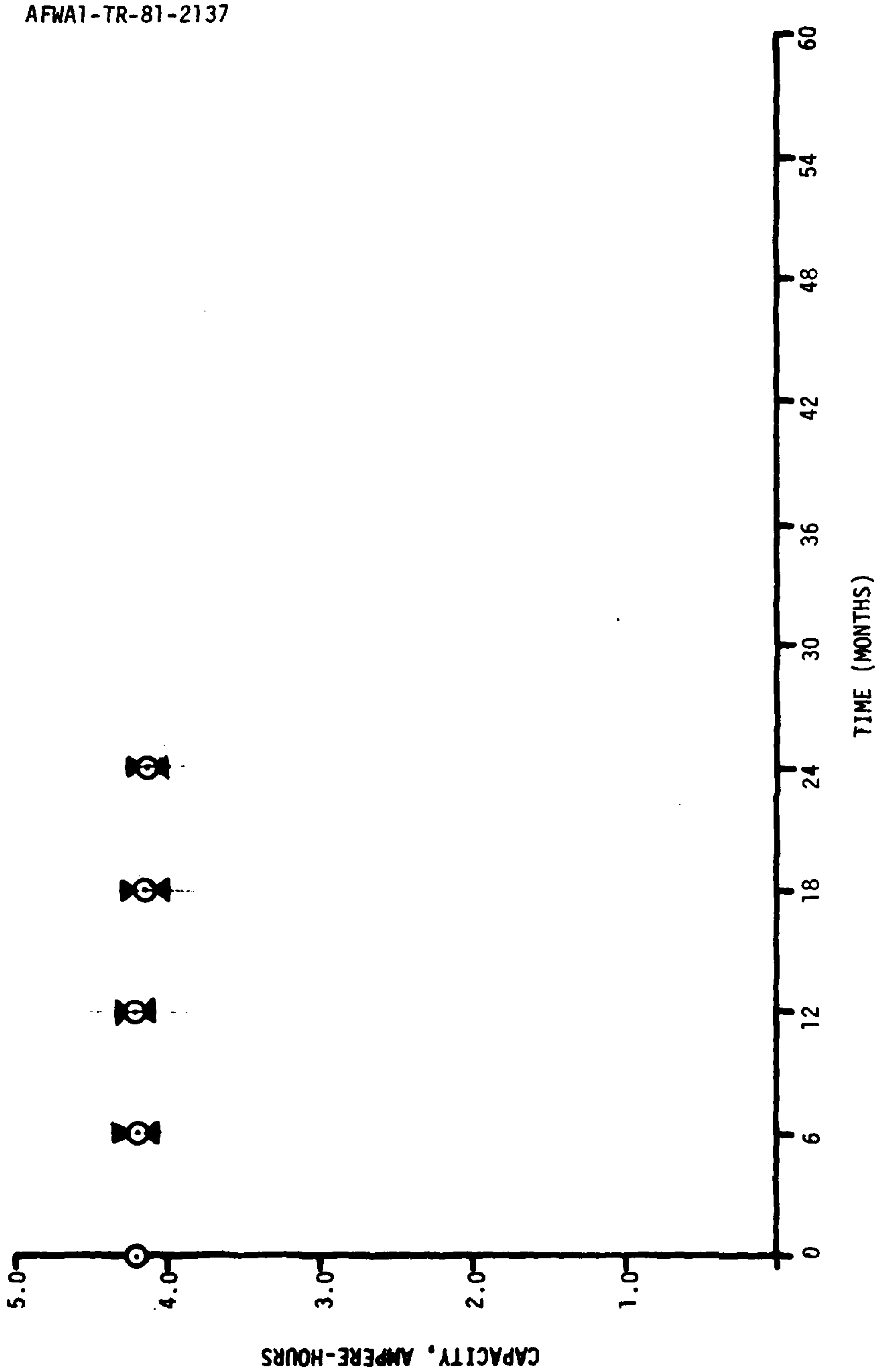

Figure 26. Capacity vs. Storage Time at Low Temperature

One other storage evaluation, a temperature cycling test, was performed for the dual purpose of comparing the performance of two different glass-to-metal seals and verifying the capability of the cells to withstand intermittent exposure/storage at 205°F. Figure 27 presents the results of this temperature cycling test. The graph on the right side of Figure 27 shows how the temperature cycling was performed on a daily basis. Overnight storage was at room temperature. At intervals of 1, 2, 3, and 4 weeks of exposure to this temperature cycling cells incorporating both types of seals (two different glass-to-metal seals) were removed and discharged at 300MA constant current. Within this environment both types of cells withstood the temperature cycling. Throughout the test, no bulging, leaking or venting was observed. Cell capacities showed only slight variation and within each data point, cell to cell variation was similar to that of one year room temperature storage. This test did verify the capability of this cell design to withstand intermittent exposure to 205°F. No difference in glass-to-metal seal performance was noted.

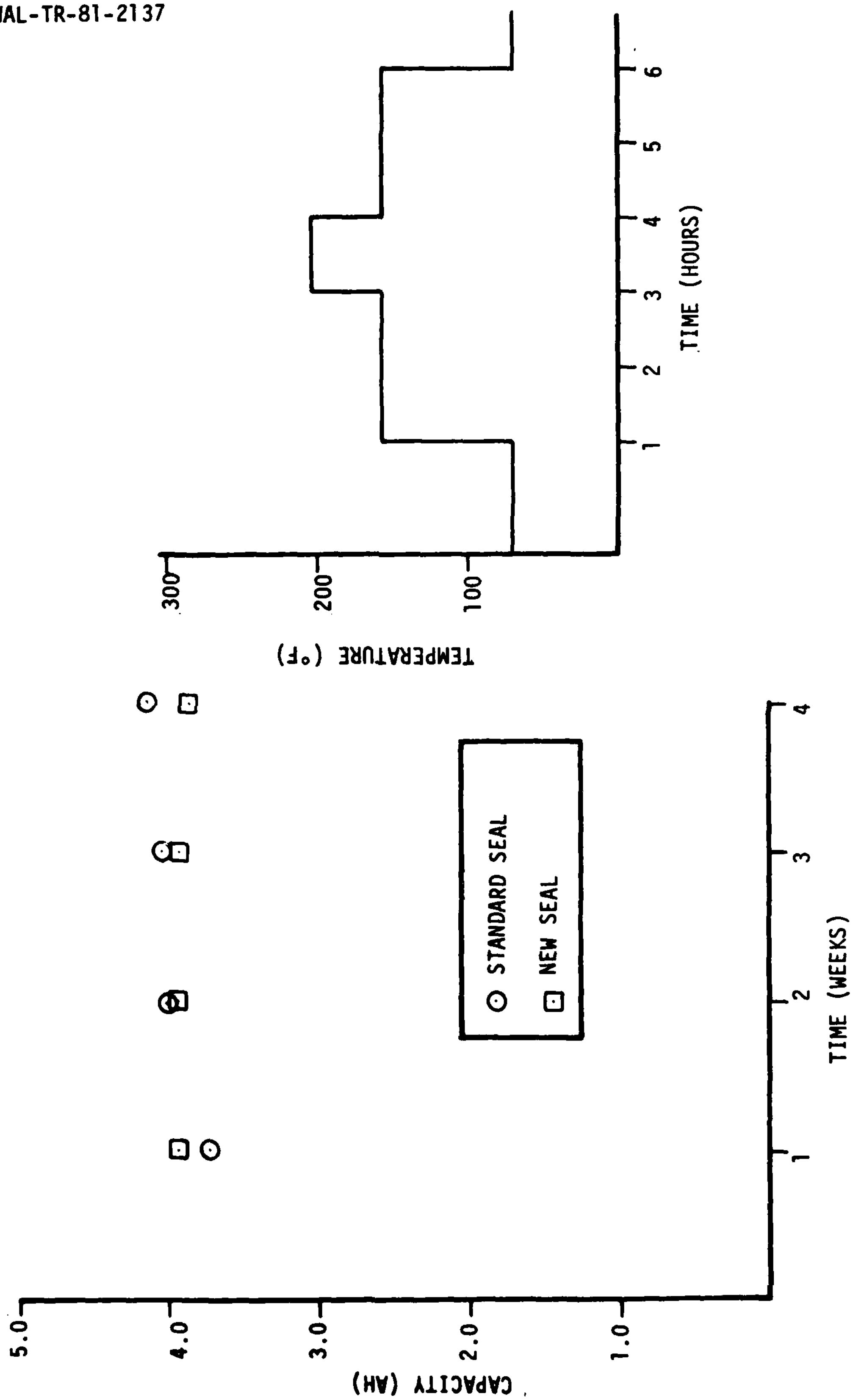

Figure 27. Capacity vs. Storage Time under Extreme Temperature Cycling

SECTION V

CONCLUSIONS

The lithium-sulfur dioxide pilot production cell developed by HPSC under an Air Force manufacturing methods technology program has been evaluated under a variety of conditions and demonstrated significantly improved performance over previous cell designs. From the evaluation of both the first engineering prototype cell and the pilot production cell, a comparison of several key characteristics was made possible. Although numerous changes were made between the two designs evaluated, certain conclusions about these design features in relation to performance can be made.

In regard to fresh cell performance under various loads at temperatures between -65°F to +140°F, the pilot production cell provided highly improved performance over the first EPC. In comparison, the pilot production cell demonstrated more uniform discharge curves over the range of loads and temperatures, a much greater low temperature operation capability, and the absence of initial voltage delay at the onset of a low temperatures. For example, at the 50MA discharge rate at -65°F, the pilot production cell provided 70% of the 4.2 ampere-hour rated capacity without voltage delay. The first EPC provided only 28% of the 4.8 rated capacity and voltage delay was significant. Performance data for the first EPC is presented in Appendix A. It is presumed that these fresh cell performance improvements in the pilot production cell are the collective results of changes in SO_2 concentration, carbon/teflon ratio, and manufacturing processes.

Another significant performance improvement observed in the pilot production cell was the capability to provide higher percentages of rated capacity at high rates of discharge. From the data presented, it can be shown that under a discharge rate of 750MA at room temperature the first EPC provided approximately 50% of rated capacity while the pilot production cell delivered 100% of rated capacity at 100MA and 43% of rated capacity under a 5.0 ampere discharge rate. This improvement in deliverable

capacity as exhibited by the pilot production cell could be at least somewhat attributed to the incorporation of a nickel grid in the lithium anode. A grid current collector of this type would conceivably enhance lithium anode utilization and provide a positive current path through the lithium anode until the end of cell life when the lithium anode has been very nearly consumed. No post mortem analyses were performed on the cells to scientifically verify this assumption.

Due to the limited testing of the first EPC, no other direct safety comparisons can be drawn. There were no abuse tests nor storage evaluations performed on the first EPC. From the data obtained on forced overdischarge testing at room temperature and at -40°F, it was demonstrated that this specific technology can accommodate cell voltage reversal at discharge currents up to 1.0 ampere with no safety hazard. At -40°F the cell showed no signs of hazardous reaction under forced overdischarge at 2.0 amperes. Again the observed behavior must be attributed to the collective changes made to the cell design.

In regard to the pilot production cell design and the verification of capability to withstand intermittent exposure to 205°F, the main contributing design feature was the expansion of the cell volume by increasing the length of the cell by approximately 16%. This resulted in a unique cell size which could withstand intermittent storage at 205°F. Generally, previous cell designs were unable to meet this requirement.

It was realized that the incorporation of a lithium-limited composition, a lithium anode current collector, a lowering of the weight percent of SO_2 in the electrolyte, and an increase in cell volume would result in a decrease in both the gravimetric and volumetric energy densities in the pilot production cell over previous designs. The first EPC demonstrated approximately 110 watt-hours/pound and 7.8 watt-hours/cubic inch while the pilot production cell provided approximately 92 watt-hours/pound and 6.0 watt-hours/cubic inch. These values represent a 16% decrease in gravimetric and a 23% decrease in volumetric energy density. These decreases were acceptable in order to realize the increase in cell safety and performance.

In conclusion, it should be stated that the data generated and discussed in this report pertains specifically to this cell technology. Subsequent studies and evaluations have shown that further improvements could be realized through changes in electrolyte composition, anode and cathode handling processes, and manufacturing techniques.

REFERENCES

1. L. J. Blagdon and B. Randall, ERADCOM Technical Report No. DELET-TR-78-0530-F, Safety Studies of Lithium-Sulfur Dioxide Cells, (1978).

2. A. N. Dey and P. Witalis, ERADCOM Technical Report No. DELET-TR-0535-F, Safety Studies of Lithium-Sulfur Dioxide Cells, (1978).

CELL DESCRIPTION

The physical characteristics of the half "D" size first engineering prototype cell are given in Table 1. It can be seen from Table 1 that the cell is cathode limited in capacity with a lithium/sulfur dioxide ratio of 1.14/1. A partial cross-sectional view of the Honeywell first engineering prototype cell is given in Figure 1. The drawing presented in Figure 1 is not specifically of a half "D" configuration but it has been included to demonstrate general construction features. The cell is a jelly-roll type construction and incorporates a glass-to-metal hermetic seal. Since the lithium-sulfur dioxide system is a high pressure system a safety vent mechanism was incorporated on the bottom of the cell. The safety vent consists of a coined area in the cell case which allows for controlled venting upon exposure to high temperature and prevents catastrophic rupture.

APPENDIX A

EVALUATION OF PROTOTYPE LITHIUM-SULFUR DIOXIDE CELLS

SUMMARY

1. PURPOSE

The purpose of this test program was to determine the performance characteristics of the half "D" size, Honeywell lithium-sulfur-dioxide first engineering prototype cell under various load and temperature conditions. The data generated under this test program is to be considered baseline performance and will be compared with simular data on the production configuration of cells when it becomes available.

2. CONCLUSIONS

The first engineering prototype of the Honeywell lithium-sulfur dioxide half "D" size cell produces capacities ranging from 4.88 ampere hours at a 50mA constant current load and room temperature to 2.46 ampere hours at a 750mA constant current load at room temperature. Under conditions of extreme temperature capacities varied from 0.42 ampere hours at -65°F and 200mA constant current load to 2.75 ampere hours at 140°F and 400mA constant current load. Voltage delay was observed in cells discharged at temperatures below -20°F and cells never reached 2.0 volts under conditions of -65°F and 400mA constant current.

TABLE A-1

PHYSICAL CHARACTERISTICS OF HALF "D" CELL
FIRST ENGINEERING PROTOTYPE

Physical	
Outside Diameter	1.324 in
Length	1.190 in
Volume	1.64 in^3
Weight	47.8 g
Case Thickness	0.017 in
Electrodes	
Cathode	
Length	16.00 in
Width	0.65 in
Thickness	0.016 in
Mix Weight	3.2 g
Cathode Area	134 cm^2
Anode (No Grid)	
Length	18.5 in
Width	0.65 in
Thickness	0.016 in
Weight	1.68 g
Capacity	6.50 AHr
Separator	
Length	19.0 in
Width	0.85 in
Weight	0.84 g
Electrolyte - 72 wt % SO_2	
Volume	15.0 cm^3
Theoretical Capacity	5.7 AHr
Cell Case and Header Materials:	304 Stainless Steel
Terminal Pin Material:	Tantalum (0.125 in O.D.)
Separator Material:	Celgard 2400 (Polypropylene)
Glass Seal:	Hermseal Type GC SO_2 Resistant Glass
Anode Lead:	316L Stainless Steel
Cathode Lead:	1145 Aluminum

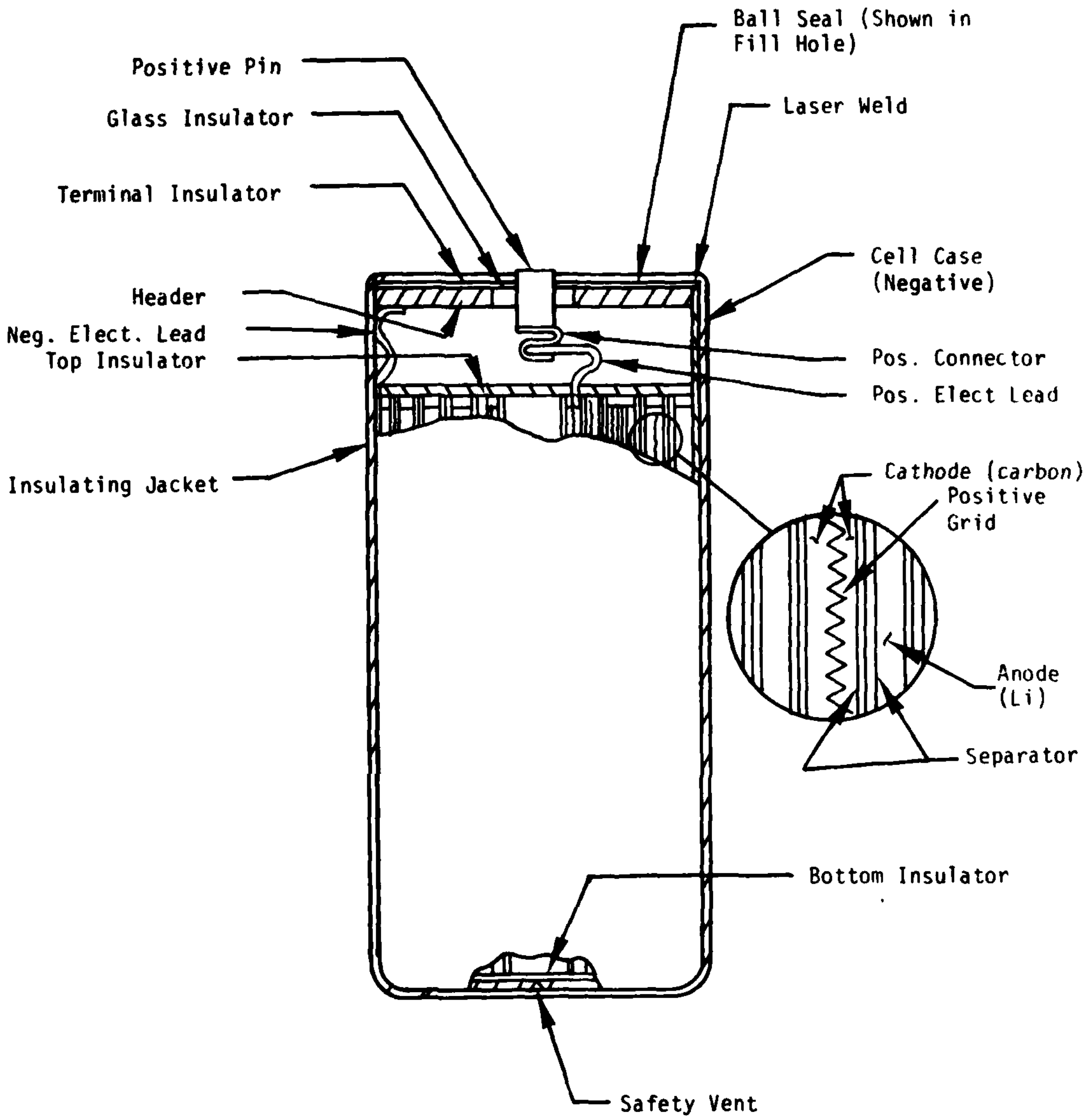

Figure A-1. Partial Cross Section of Honeywell First Engineering Prototype Cell

TEST CONDITIONS

1. TEST MATRICSES

The Honeywell half "D" size first engineering prototype cells were discharged to a 2.0 volt cutoff under various constant current loads at different temperatures. Two test matreses were used to determine the cells' electrical performance.

The first test performed was a characterization of cell performance under various constant current discharge loads at room temperature. Table 2 presents the loads used and the number of cells used for each test. Since this was first test run, the objective of this test was to determine relative ampere-hour capacity under various load conditions.

TABLE A-2

TEST MATRIX FOR CAPACITY VS. DISCHARGE CURRENT TEST

CONSTANT CURRENT LOAD	NUMBER OF CELLS
50mA	6
100mA	6
200mA	6
350mA	6
500mA	6
750mA	6

The second evaluation performed on the first engineering prototype cells was a characterization of ampere-hour capacity under various discharge currents at various temperatures. This evaluation generated a family of curves that depict capacity loss as a function of temperature. Table 3 (Page 6) presents the temperature and discharge load conditions and the number of cells used in each condition for this evaluation.

TABLE A-3

TEST MATRIX FOR CAPACITY VS. TEMPERATURE AND DISCHARGE CURRENT TEST

	Discharge Currents			
Temperature °F	50mA	100mA	200mA	400mA
140	4	6	6	6
110	--	--	6	6
100	--	--	6	--
90	6	6	6	6
75 (room)	6	6	6	6
50	--	--	6	--
30	6	6	6	6
0	6	6	6	6
-20	--	--	6	6
-40	4	6	6	6
-50	--	--	6	4
-65	--	--	6	--

2. TEST EQUIPMENT, PROCEDURES, AND SAFETY PROVISIONS

Lithium sulfur dioxide cells used in this evaluation were received in January 1978 from Honeywell Power Sources. An initial cell inspection was performed which included a measurement of open circuit voltage (2.97 volts) and a visual inspection for structural defects, seal integrity, corrosion, leakage and possible damage during shipment. All cells were logged in and assigned cell numbers. Cells were stored at room ambient temperature in a random orientation within an OSHA approved Protectoseal storage cabinet. Cells were kept in their original shipping containers which included being sealed in plastic bags immersed in vermiculite within cardboard drums.

All testing was performed in Tenney "5" temperature chambers. These chambers have been adapted to allow proper ventilation without opening (exposure to personnel). This was accomplished through the use of a positive pressure air line in one port of the chamber and a one-way relief valve through another port which is vented to the outdoors. Constant current discharge was performed by a Trygon model HR40-750 (max 40V, 750mA) power supply and a Cenco variable resistor. Figure 2 is a diagram of the circuit used. A 1.0 amp, 50mV shunt was used for measuring current. Discharge tests were monitored through an automatic, computer integrated battery testing rack with automatic scanning and cut-off capabilities. The voltages of cells were scanned during discharge and automatically recorded. A cut-off voltage of 2.0 volts was employed to insure that the cells were not driven into reverse.

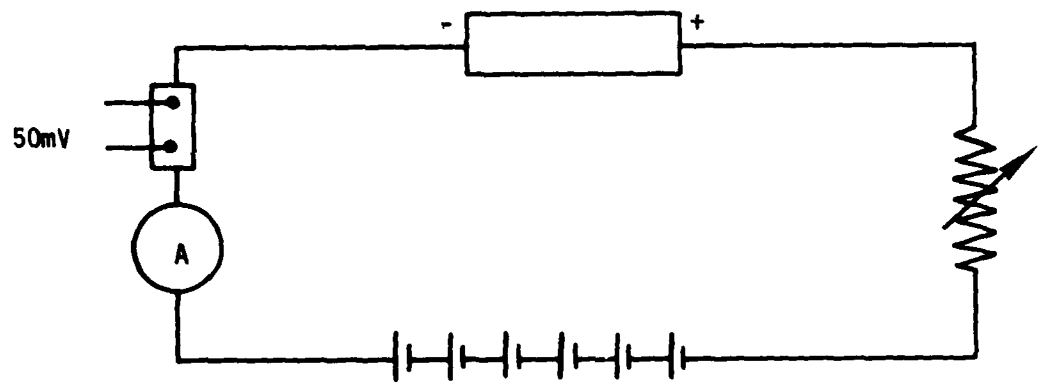

Figure A-2. Test Circuit

TEST RESULTS AND DISCUSSION

The capacity of the cells tested under various constant current loads is presented in Figure A-3. It should be noted that in Figure A-3 that the variation in cell capacities (shown as plus or minus one standard deviation) is depicted as a vertical line. The dot in the vertical line represents the average capacity of all cells tested under that condition.

It can be seen from Figure A-3 that the cell capacity decreased approximately 50% as a result of increasing the constant current load from 50mA to 750mA. In general a decrease in capacity with increasing load is an expected result. It should also be noticed that the variation in cell capacities under specific loads increased with increasing load. This implies that these cells did not have good uniform high rate capability. Uniformity of results is expected to increase in the production lot of cells to be manufactured at the end of the AF manufacturing technology program. These cells were essentially hand made and cannot be expected to exhibit the uniformity of a production quantity.

The capacity of cells tested at various temperatures under various constant current loads is presented in Figure 4. Values reported are the average of all cell capacities tested under the specific condition. No variation data are presented, however, it was noted from the raw data that cell capacity variation increased at lower temperatures and higher rate.

Figure 4 indicates that the maximum cell capacity can be obtained at room temperature for 50 and 100mA loads and a temperature slightly higher ($\sim$100°F) for higher rates (200 and 400mA). This maximum decreases significantly at temperatures below +30°F and above 110°F. These cells were dramatically effected by temperature extremes and especially by low temperature. Cathode structure and electrolyte composition are assumed to be the most influential parameters on this behavior. Changes in these parameters will be made on subsequent lots of cells and comparative data is not yet available.

It is not indicated on Figure A-4 that a significant voltage delay did exist for discharges below -20°F. Voltage delay is defined as the time required between the onset of the load and the time the cell voltage reaches 2.0 volts. Voltage delay times were found to increase from a few seconds at -20°F to several minutes at -65°F. Cells discharged at 400mA and -65°F never reached 2.0 volts and the test was terminated. This phenomenon could play a detrimental role in actual in-field use and will be studied further at a later time. It is hoped that this delay time may be decreased in subsequent lots of cells since the vendor is aware of the problem and is taking steps to diminish or eliminate voltage delay.

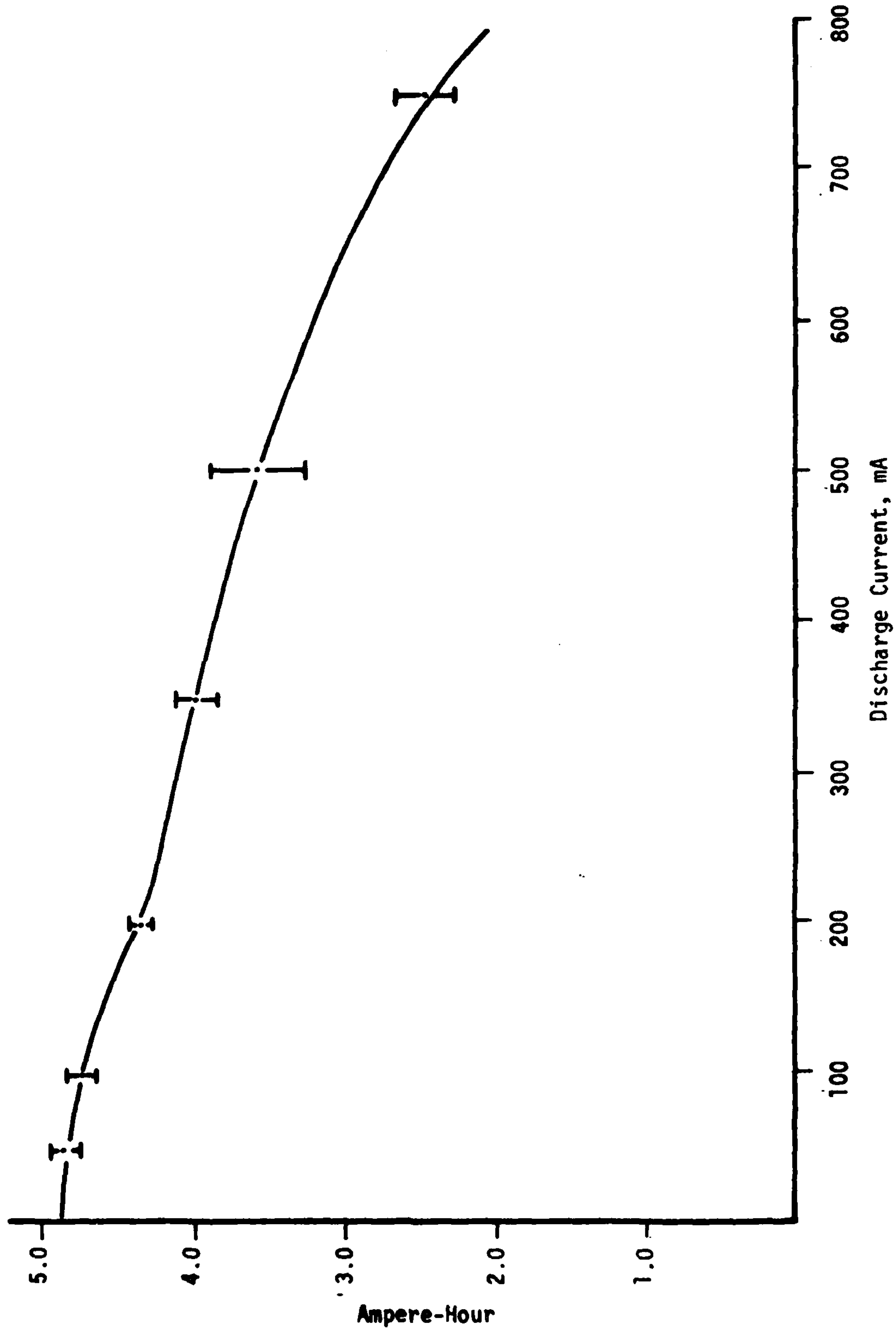

Figure A-3. Capacity vs. Various Constant Current Loads at Room Temperature

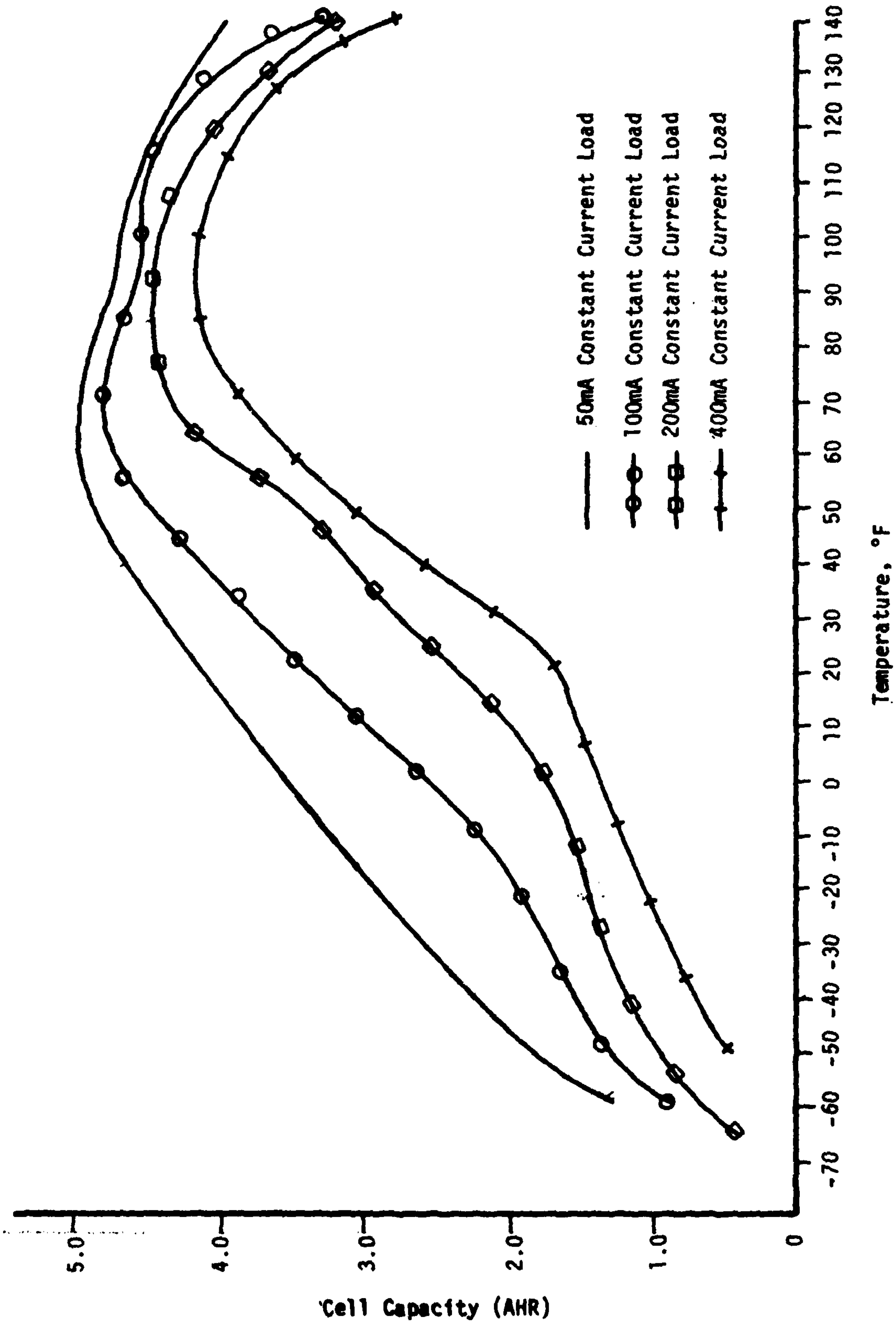

Figure A-4. Capacity vs. Temperature at Various Constant Current Loads

APPENDIX B

Some Graphic Statistical Data for both First Engineering Prototype and Pilot Production Cells under various conditions of discharge rate and temperature.

NOTE: The drawing to the left is used in the following curves to represent a specific data point. The dot represents the arithmetic mean of the cells. The ends of the propeller represent one positive and one negative standard deviation from the mean.

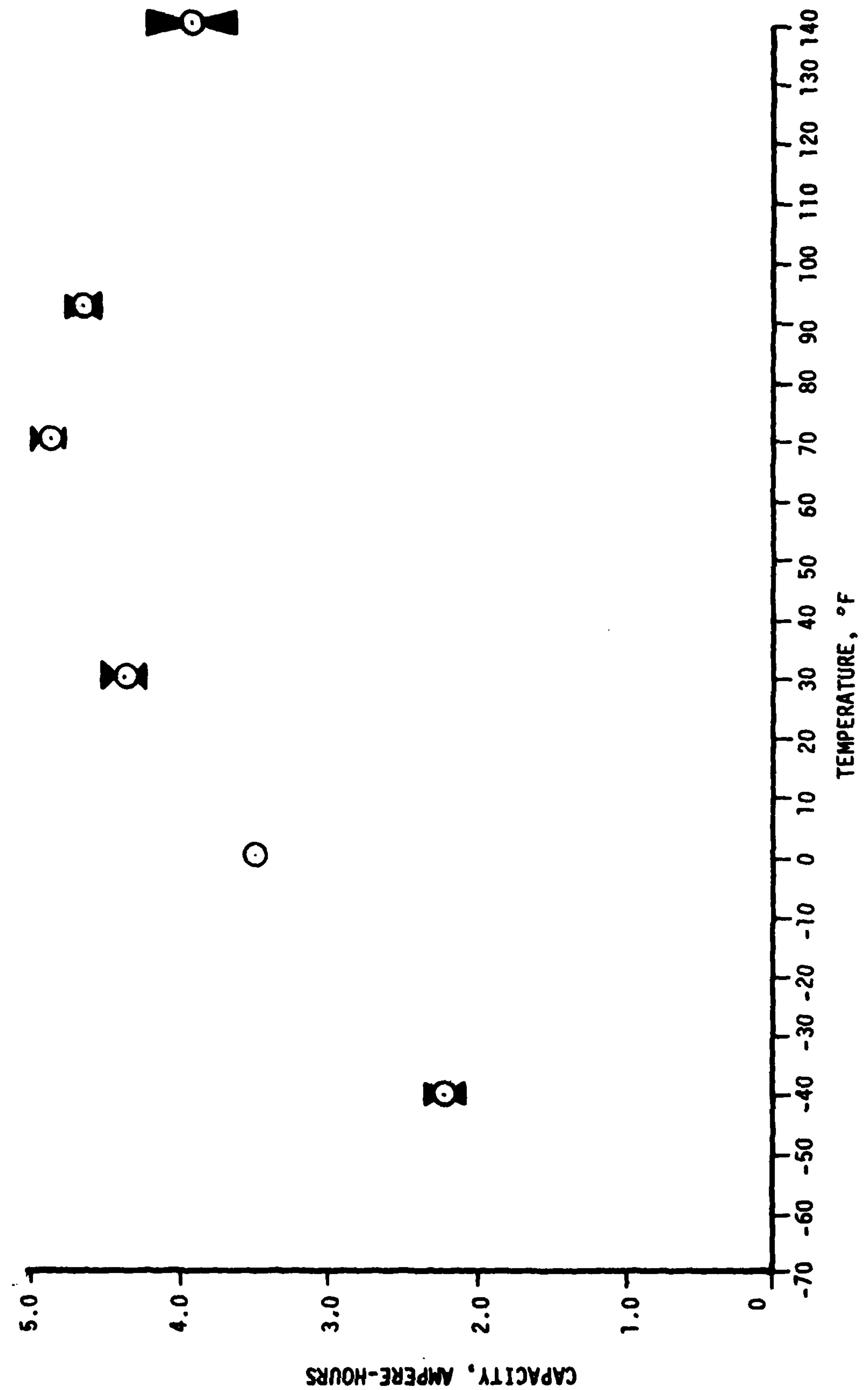

Figure B-1. Fresh Cell Performance Under 50mA Discharge (First Engineering Prototype)

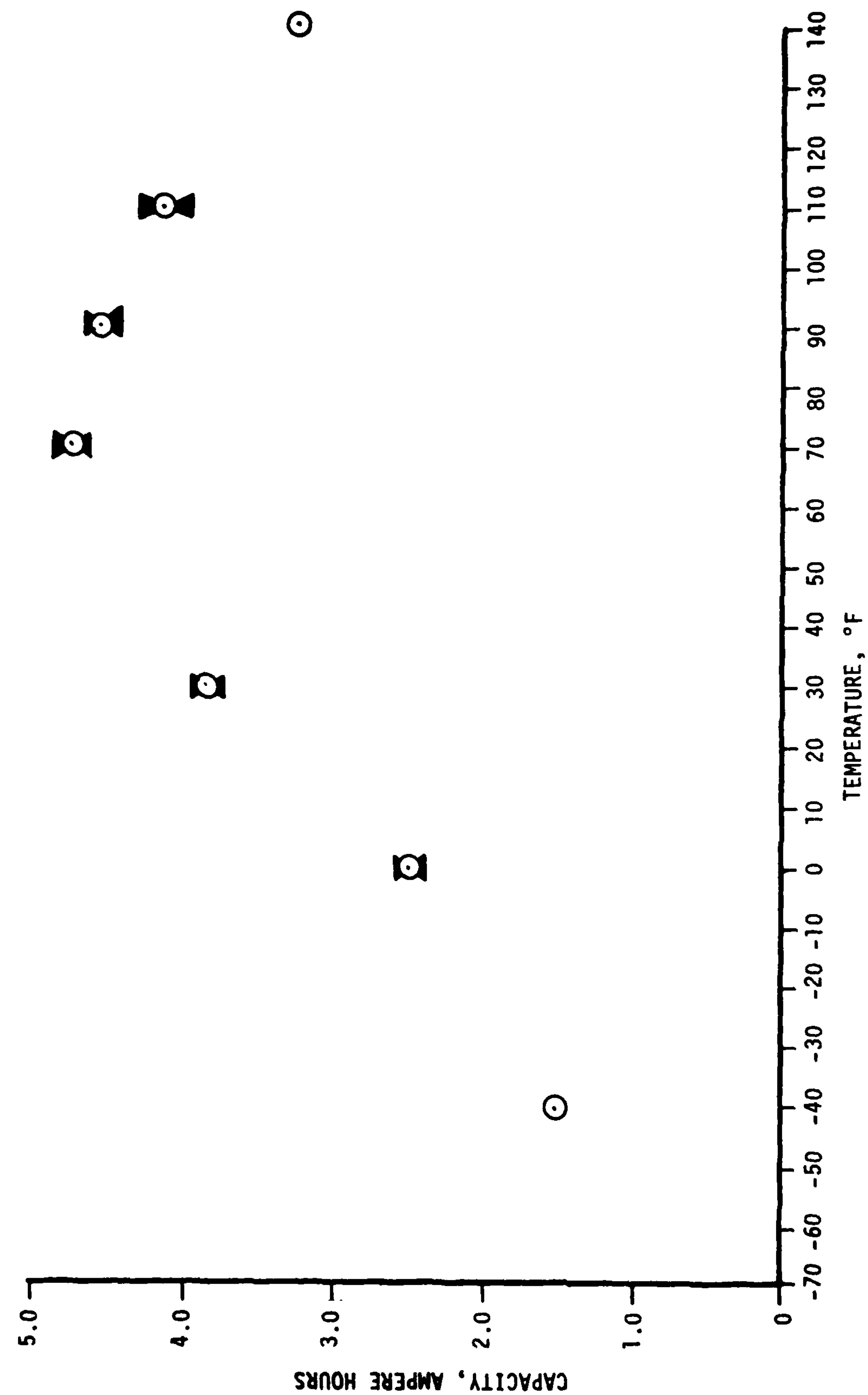

Figure B-2. Fresh Cell Performance Under 100mA Discharge (First Engineering Prototype)

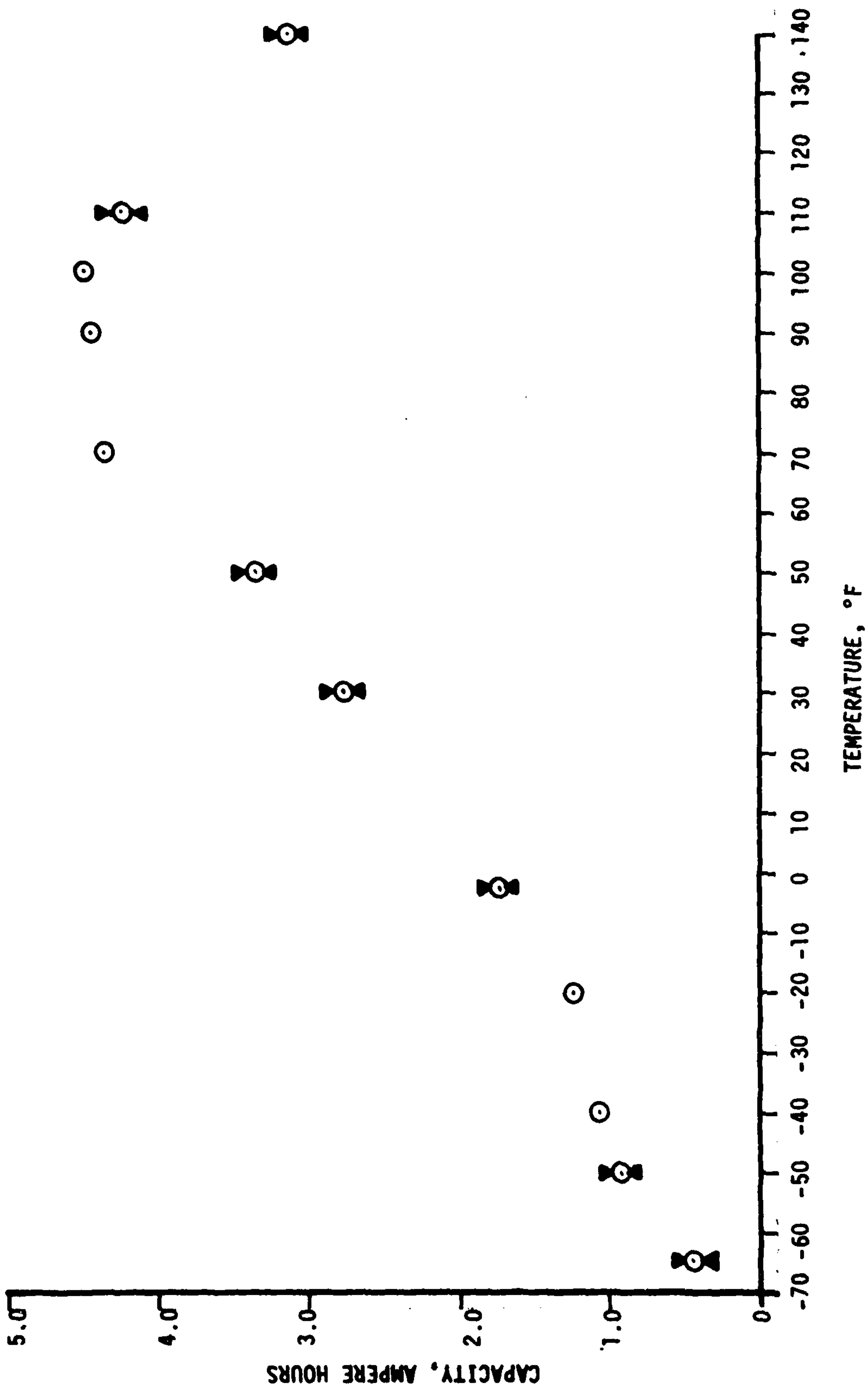

Figure B-3. Fresh Cell Performance Under 200mA Discharge (First Engineering Prototype)

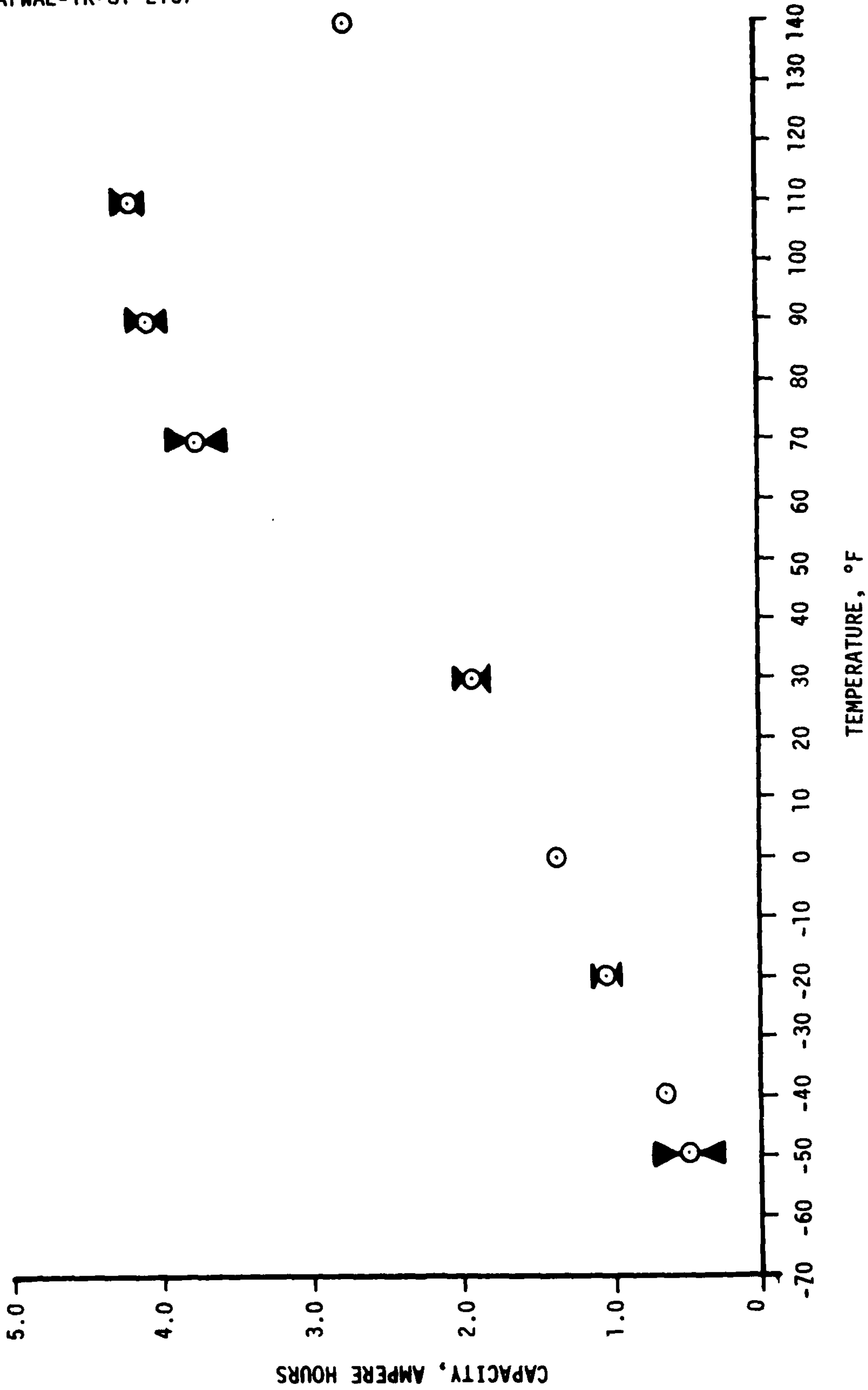

Figure B-4. Fresh Cell Performance Under 400mA Discharge (First Engineering Prototype)

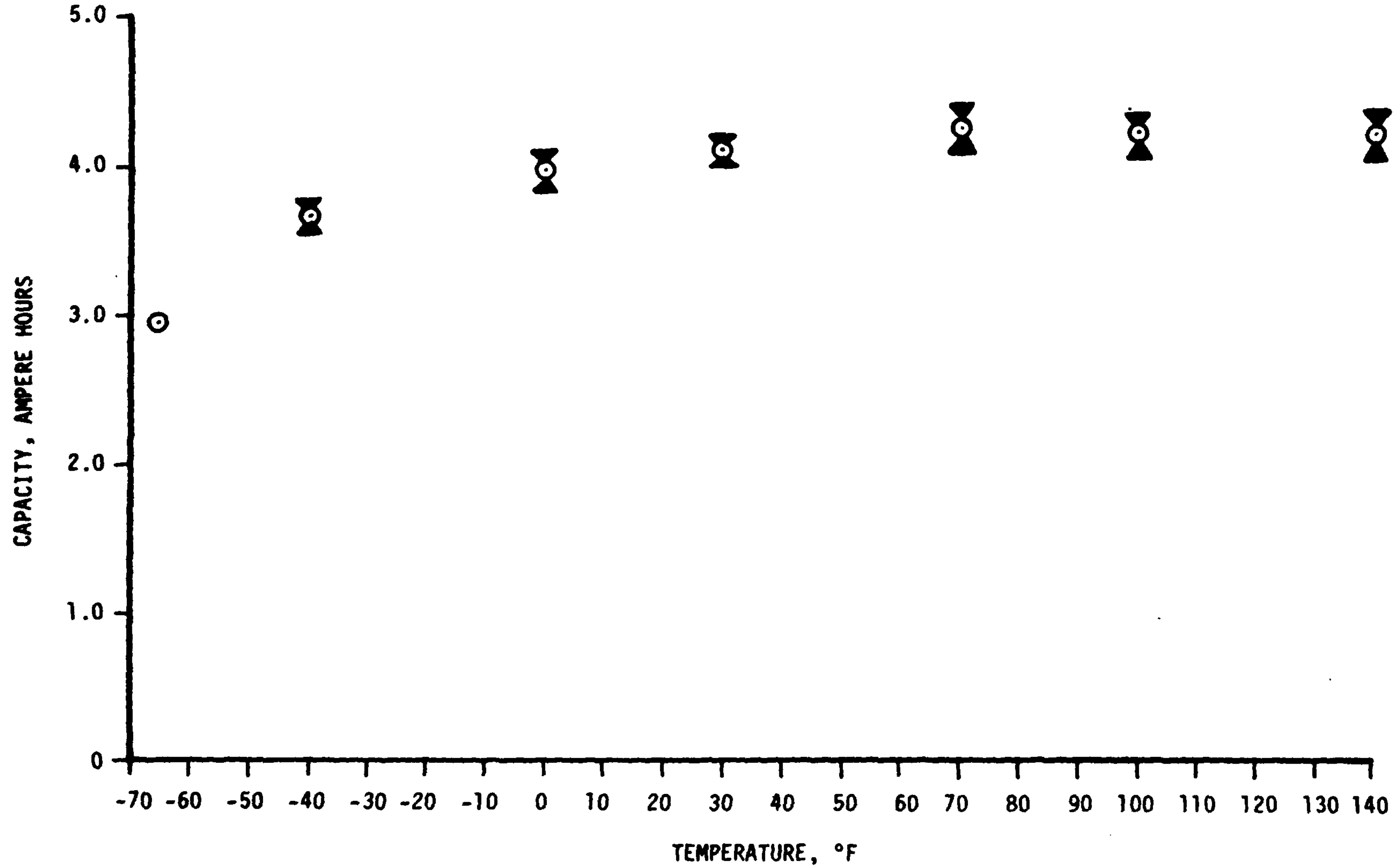

Figure B-5. Fresh Cell Performance Under 50mA Discharge (Pilot Production Cells)

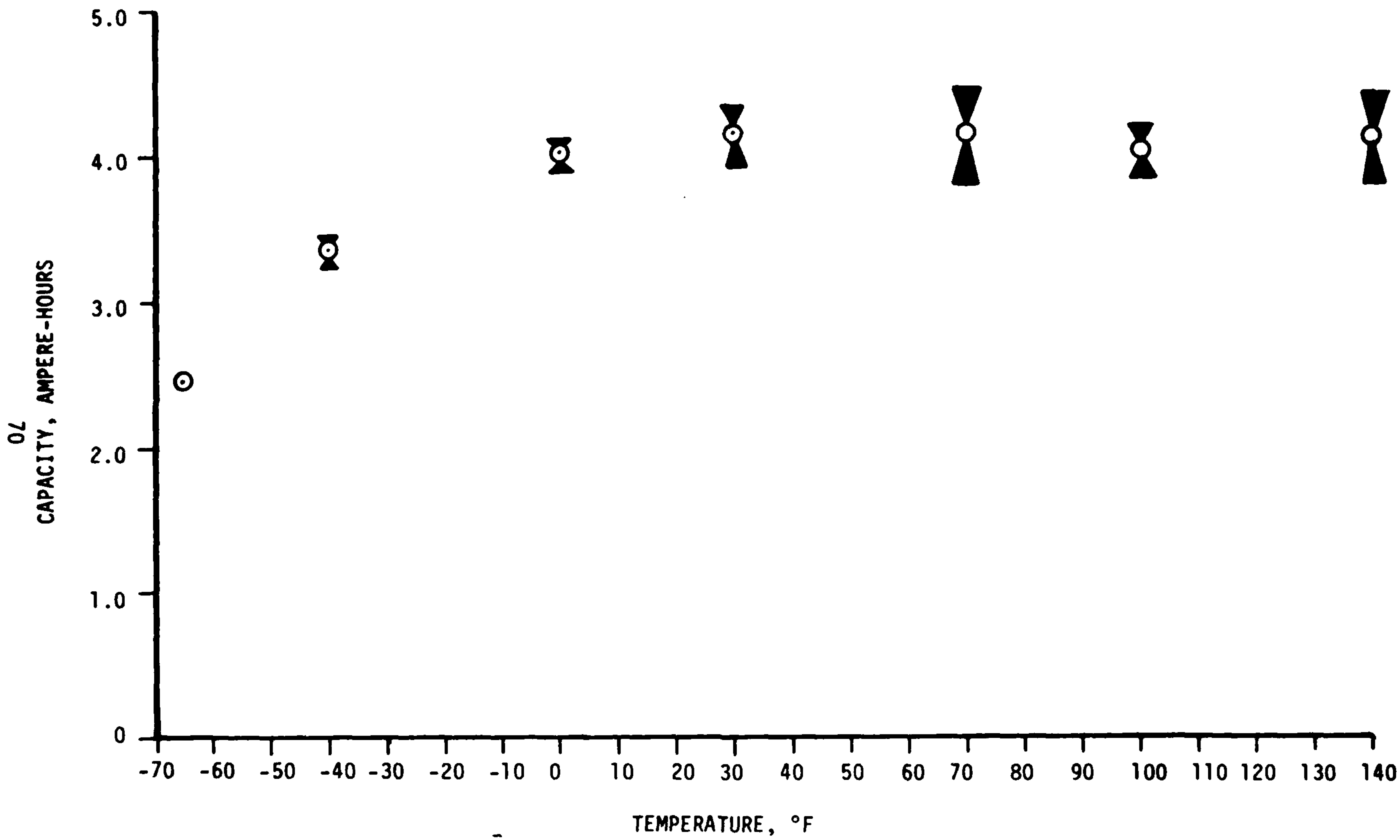

Figure B-6. Fresh Cell Performance Under 100mA Discharge (Pilot Production Cells)

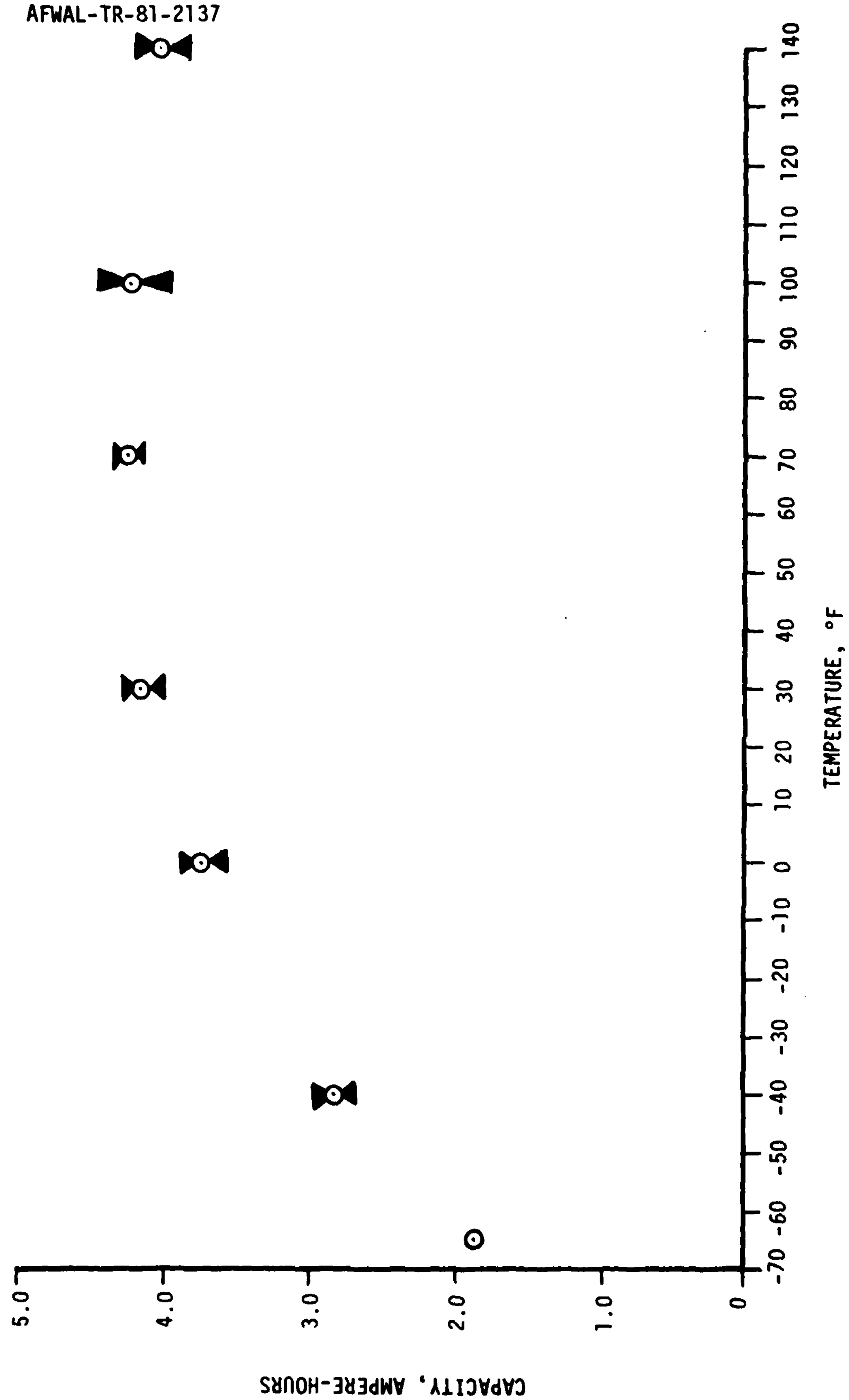

Figure B-7. Fresh Cell Performance Under 200mA Discharge (Pilot Production Cells)

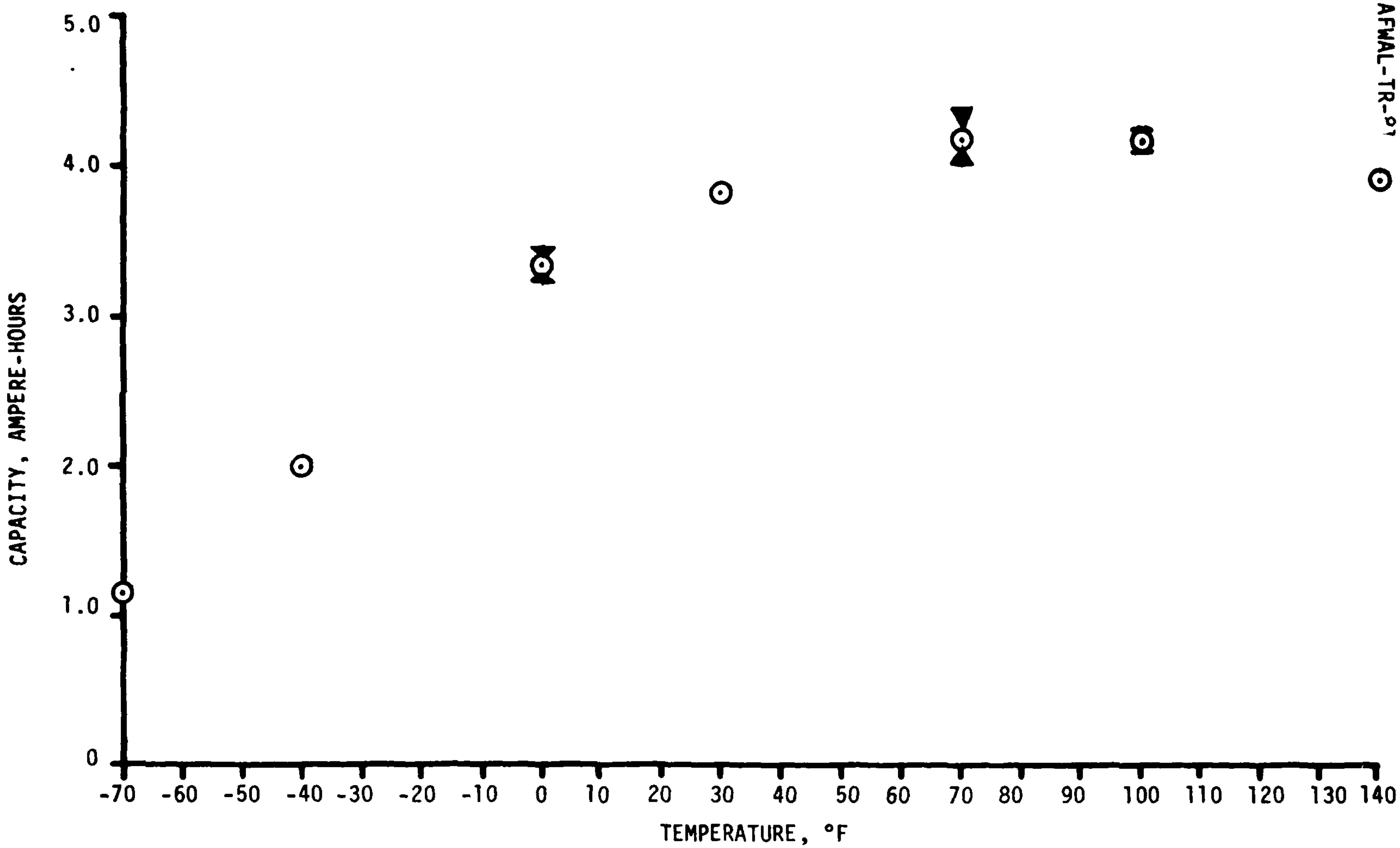

Figure B-8. Fresh Cell Performance Under 400mA Discharge (Pilot Production Cells)

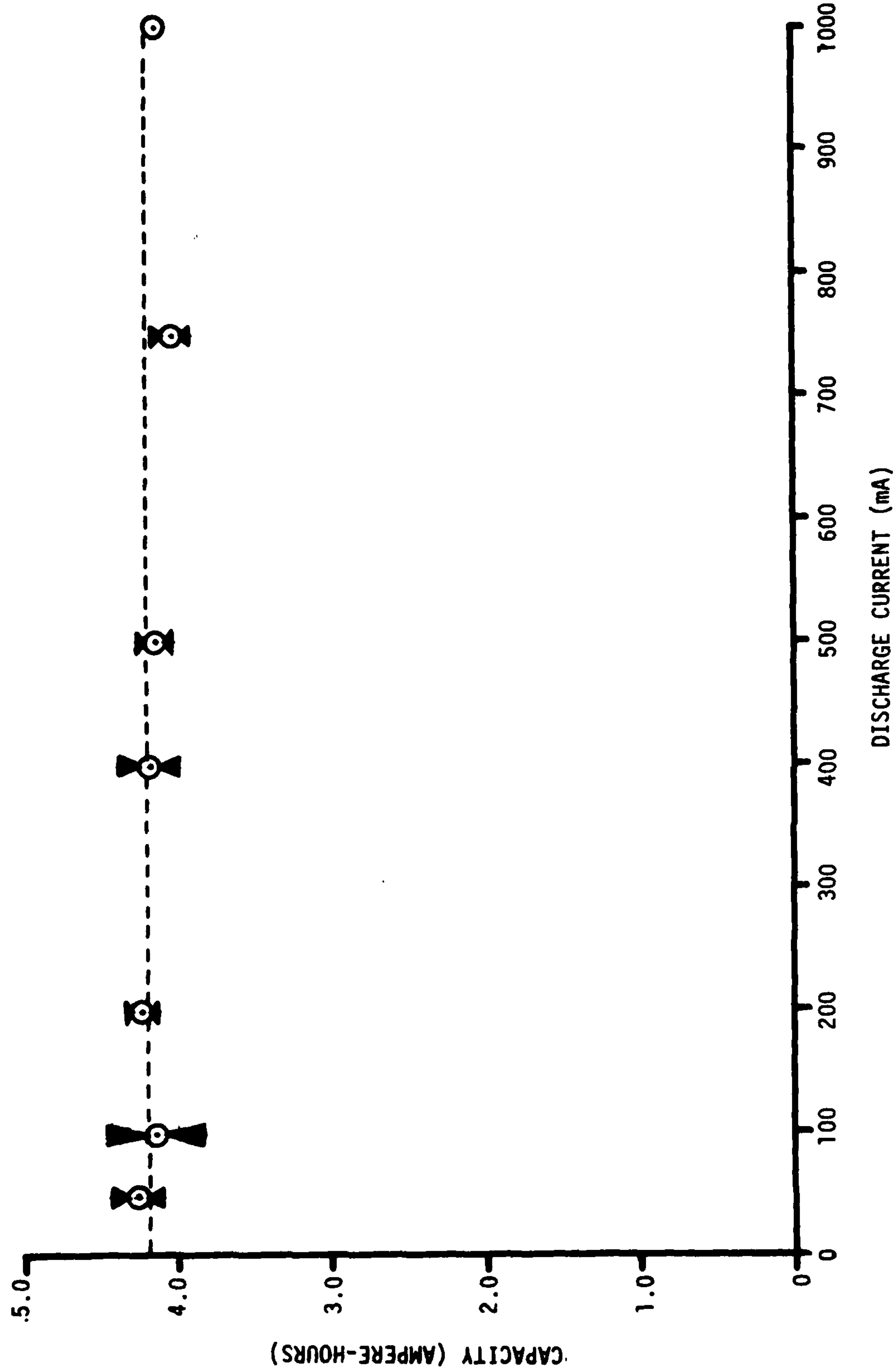

Figure B-9. Capacity vs. Discharge Load at Room Temperature (Production Cells)

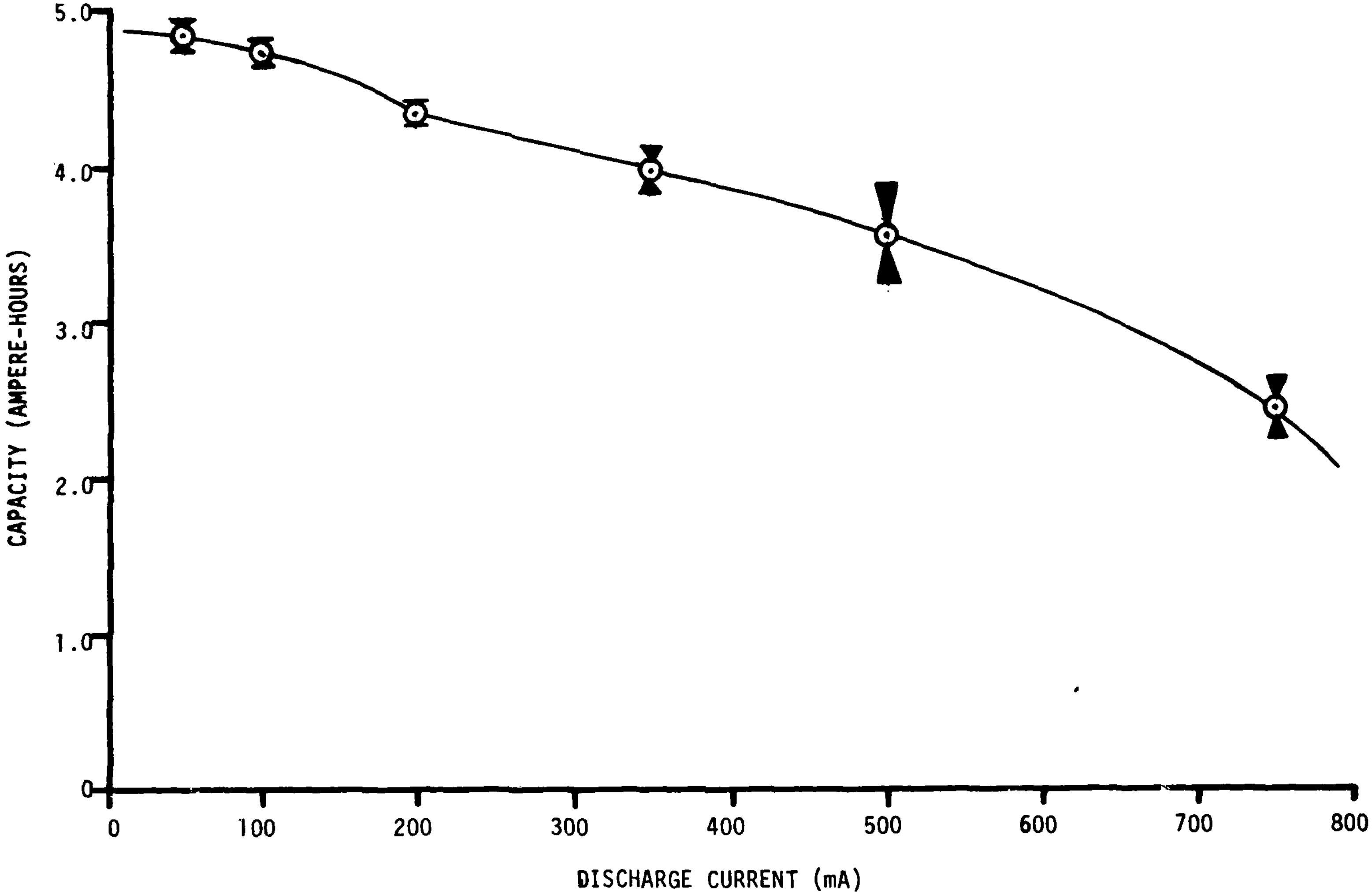

Figure B-10. Capacity vs. Discharge Load At Room Temperature (First Engineering Prototype)

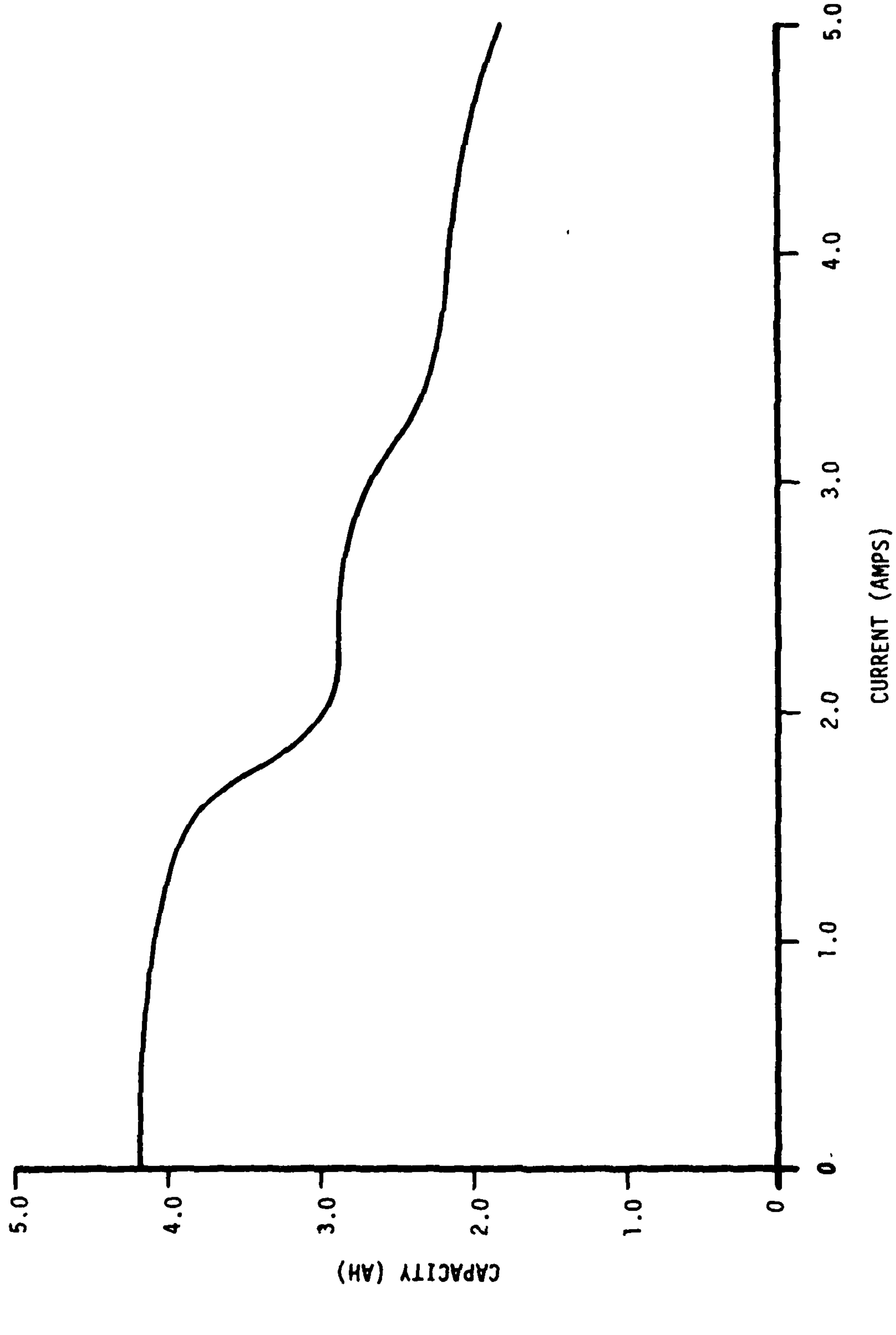

Figure B-11. Capacity vs. Rate of Discharge At Room Temperature (Pilot Production Cells)

APPENDIX C

COMPUTER PLOTS OF THE HIGH TEMPERATURE STORAGE TEST

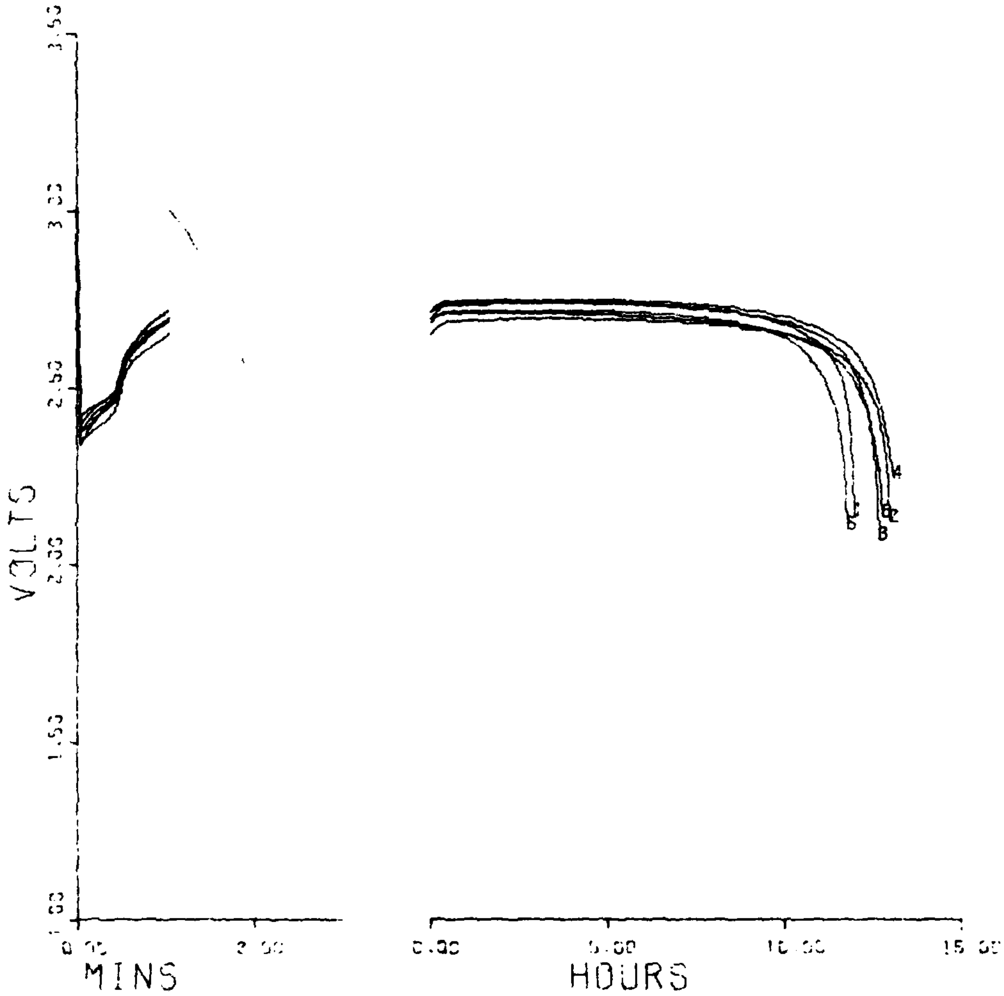

Figure C-1. Computer Plot - HW .6D LI-SO2 Cells,
HTS: 1 Month: 300 MA DISCH At 70 F

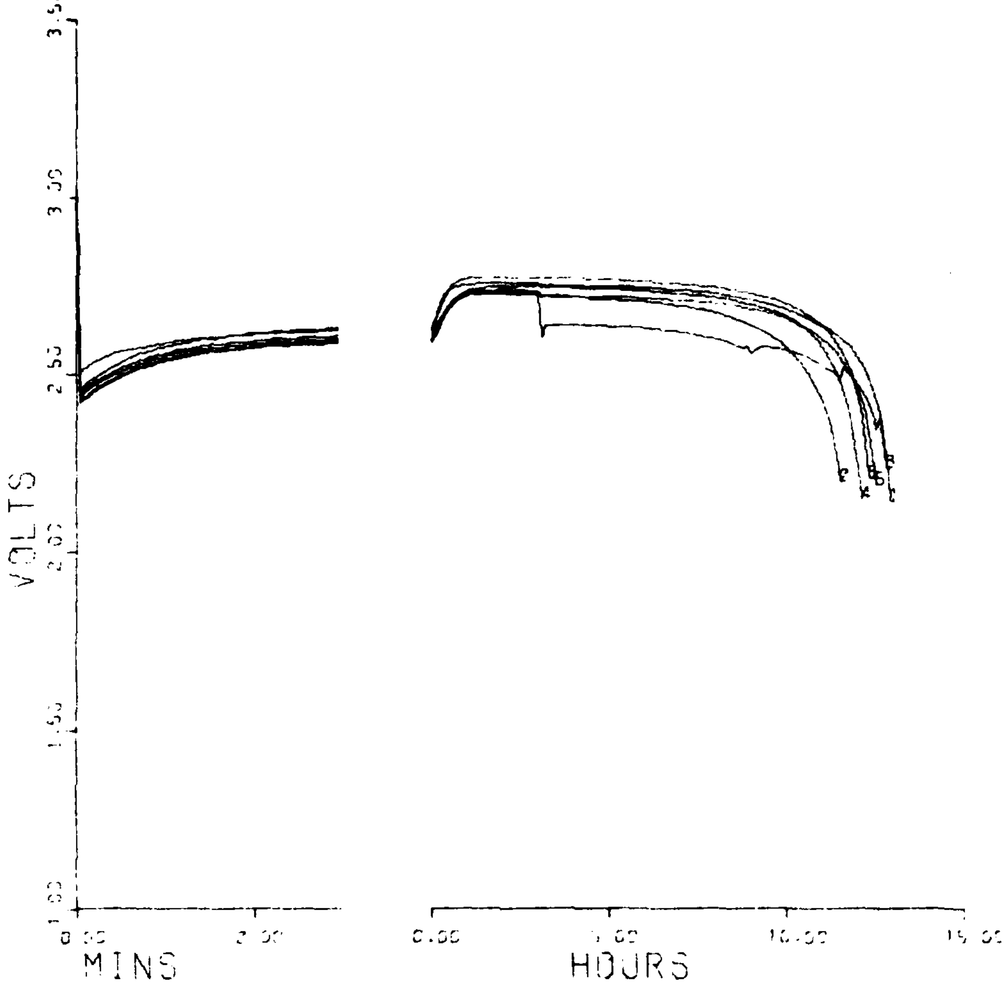

Figure C-2. Computer Plot - HW .6D LI-SO2 Cells
HTS: 2 Months: 300 MA DISCH At 70 F

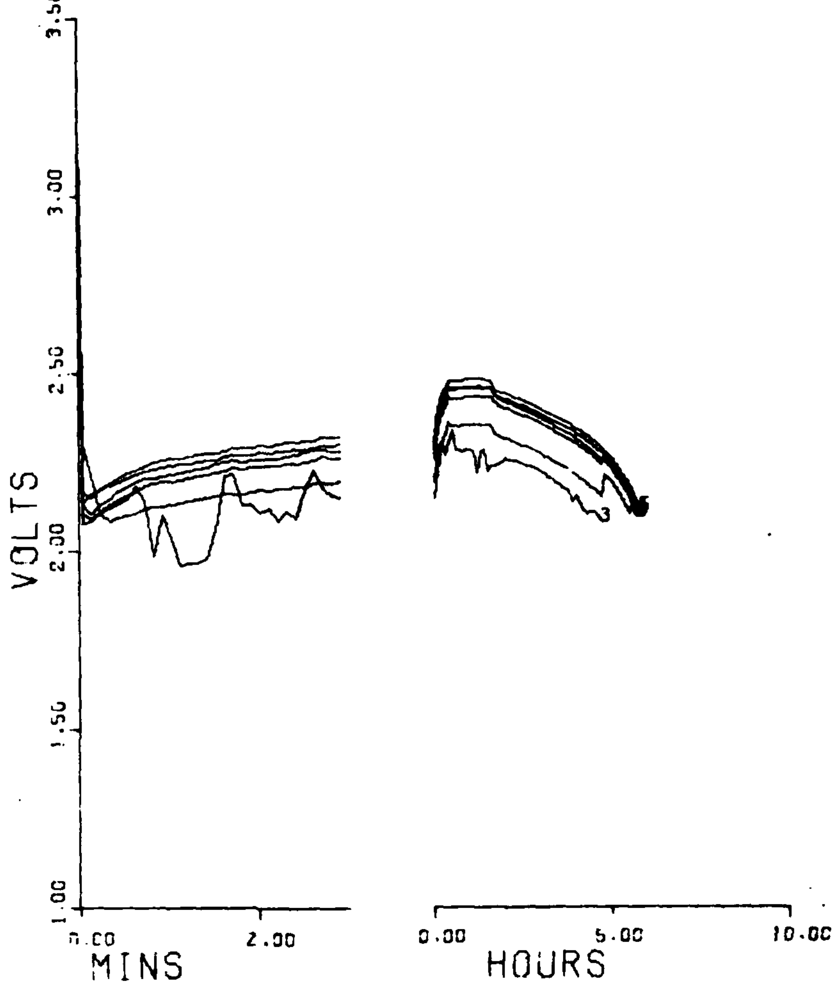

Figure C-3. Computer Plot - HW .6D LI-SO2 Cells
HTS: 2 Months: 300 MA DISCH At -40 F

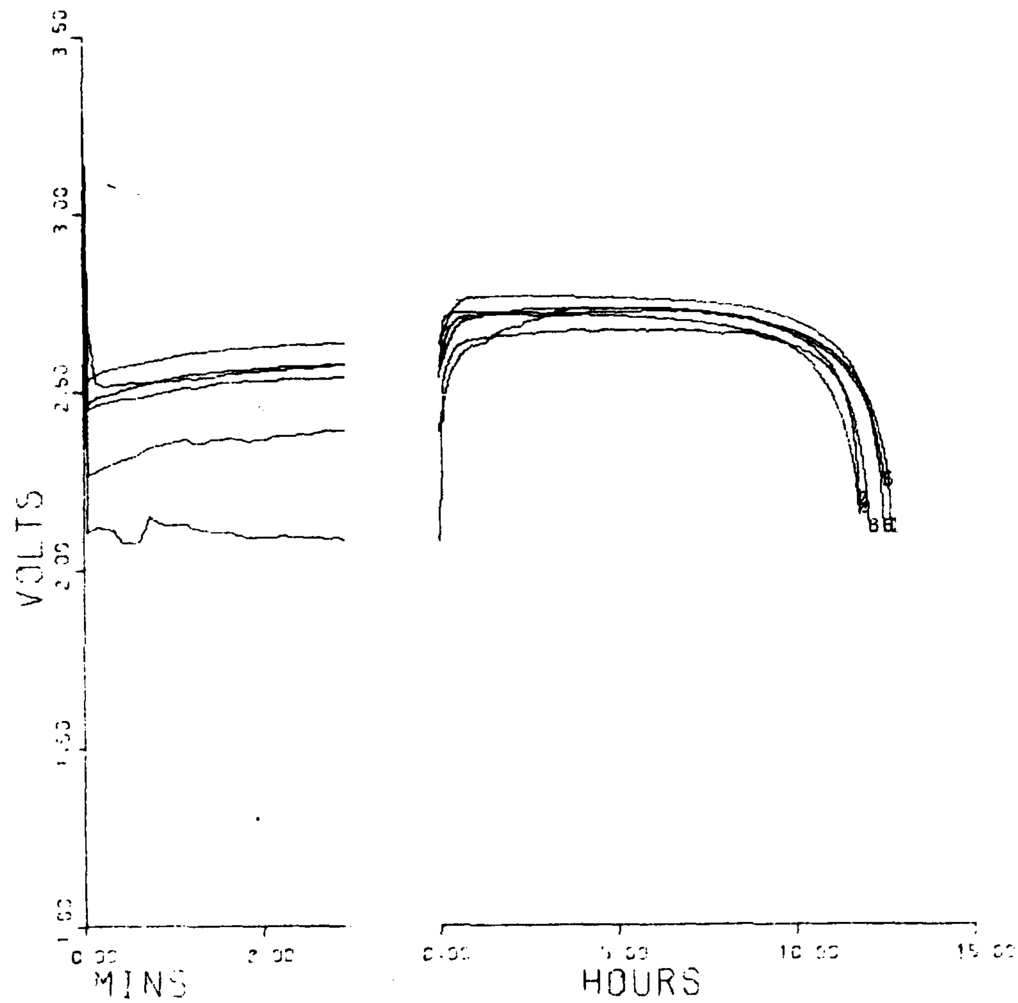

Figure C-4. Computer Plot - HW .6D LI-SO2 Cells
HTS: 3 Months: 300 MA DISCH At 70 F

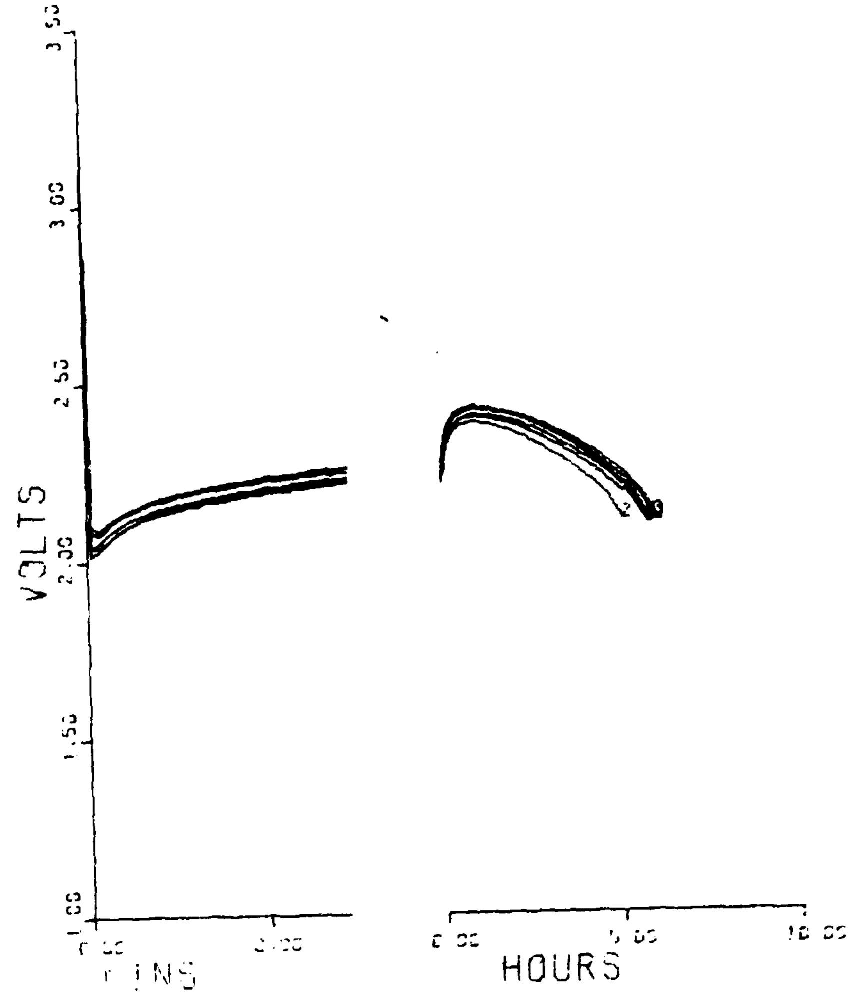

Figure C-5. Computer Plot - HW .6D LI-SO2 Cells
HTS: 3 Months: 300 MA At -40 F

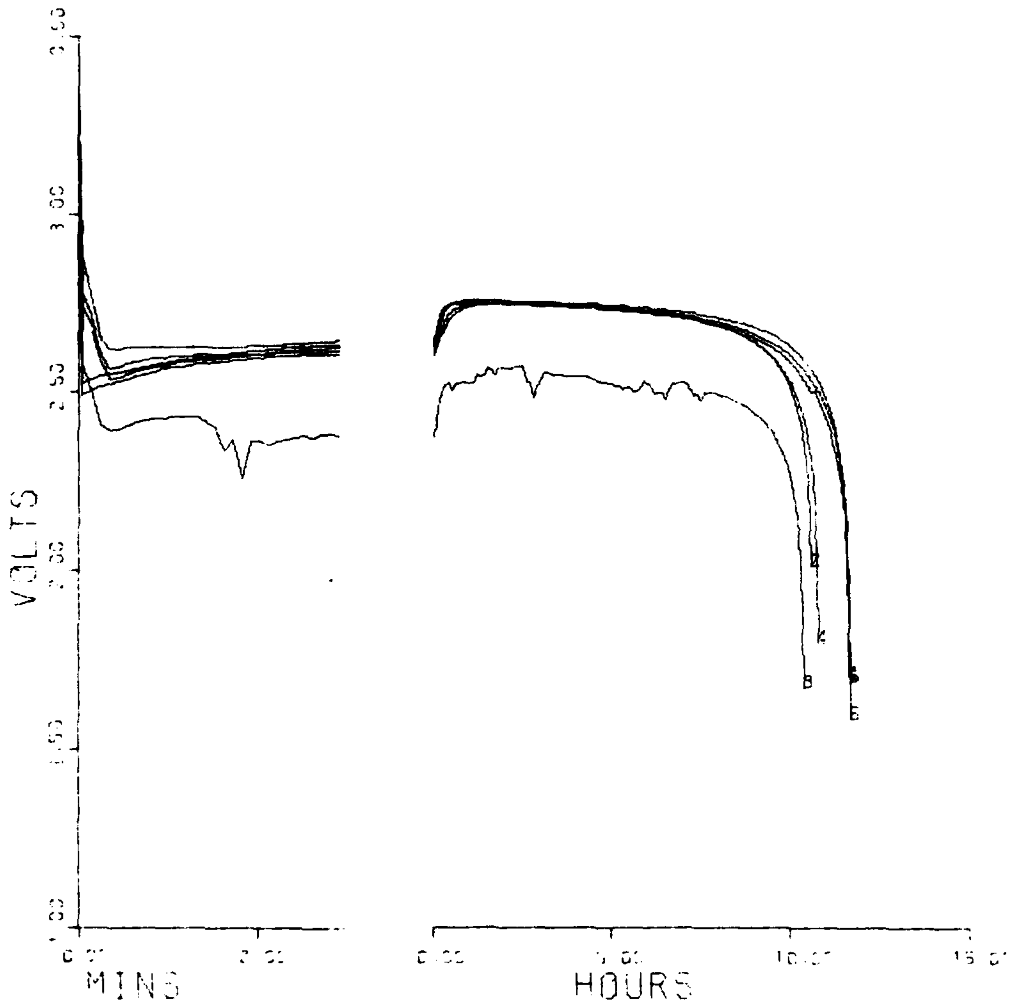

Figure C-6. Computer Plot - HW .6D LI-SO2 Cells
HTS: 4 Months: 300 MA DISCH At 70 F

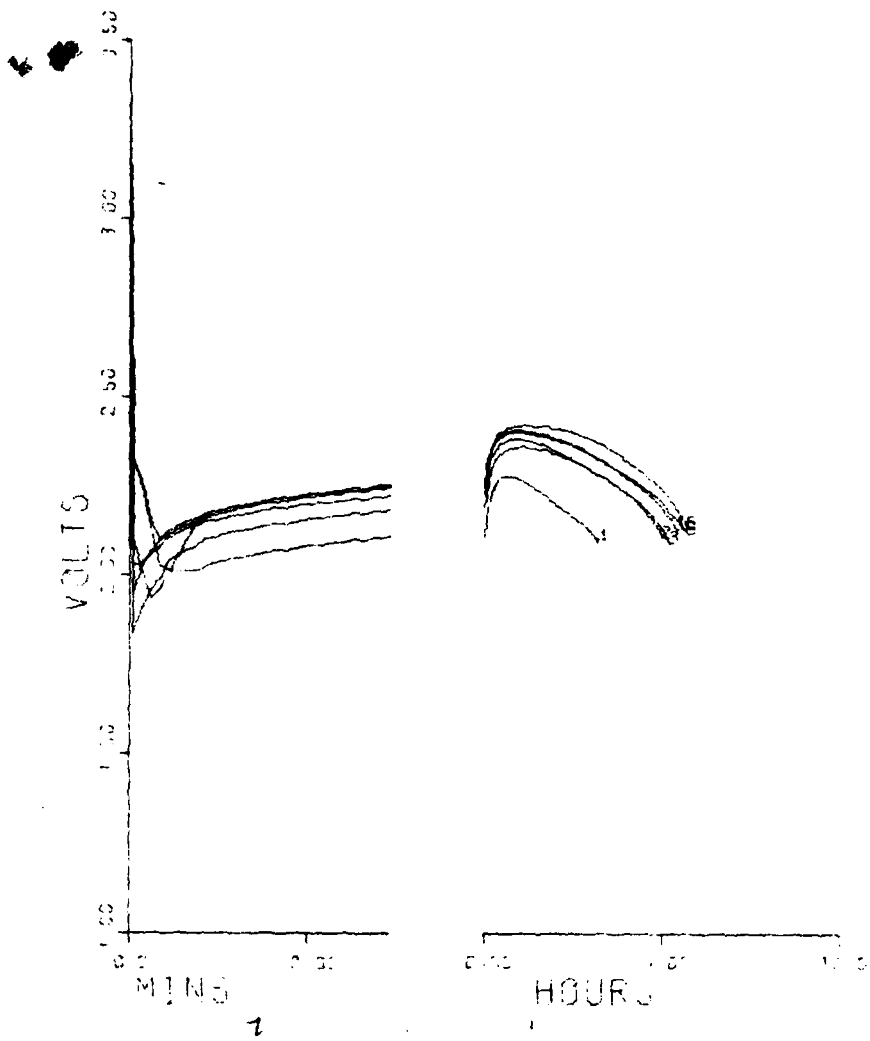

Figure C-7. Computer Plot - HW .6D LI-SO2 Cells
HTS: 4 Months: 300 MA DISCH At -40 F

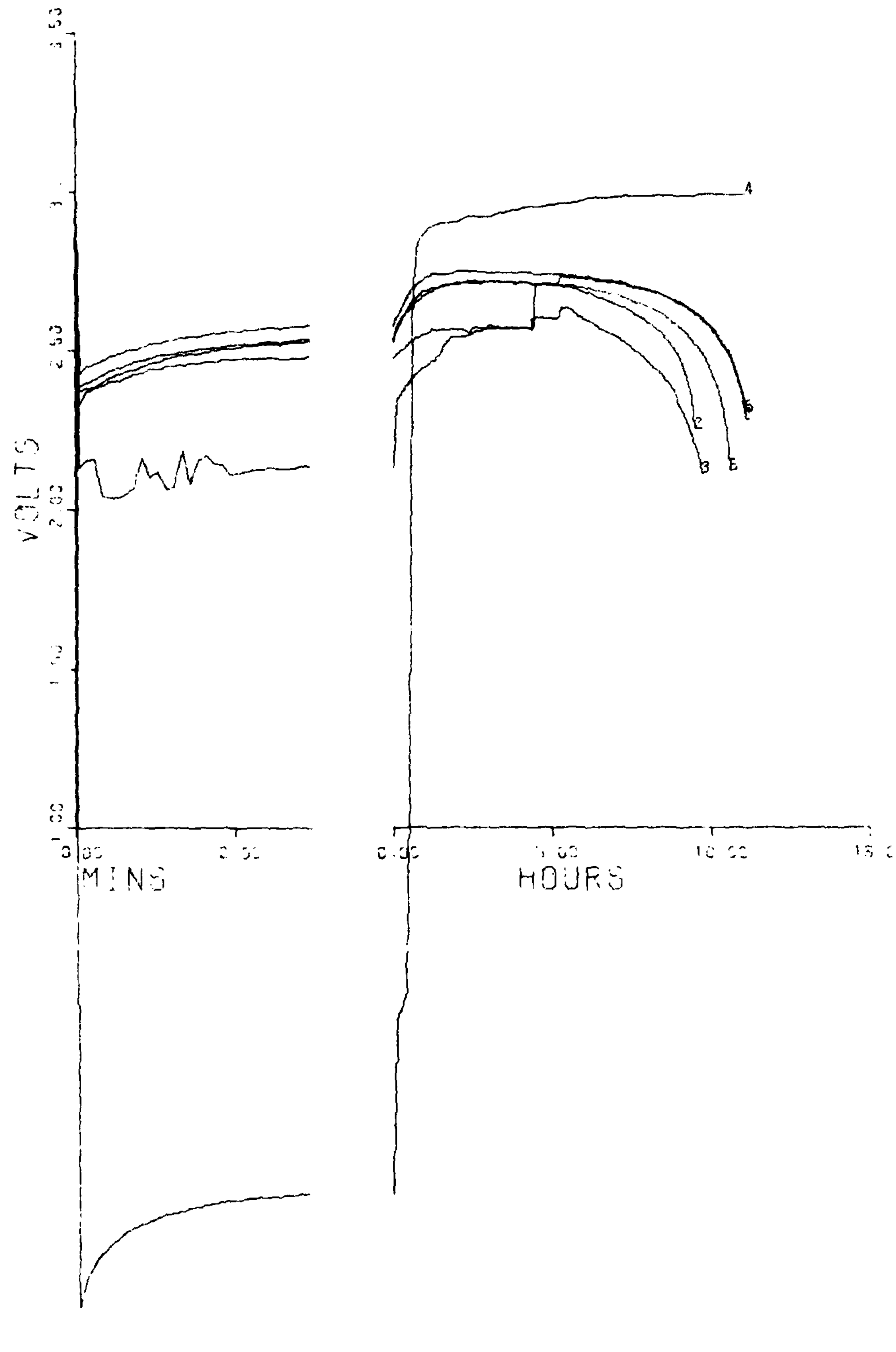

Figure C-8. Computer Plot - HW .6D LI-SO2 Cells
HTS: 5 Months: 300 MA DISCH At 70 F

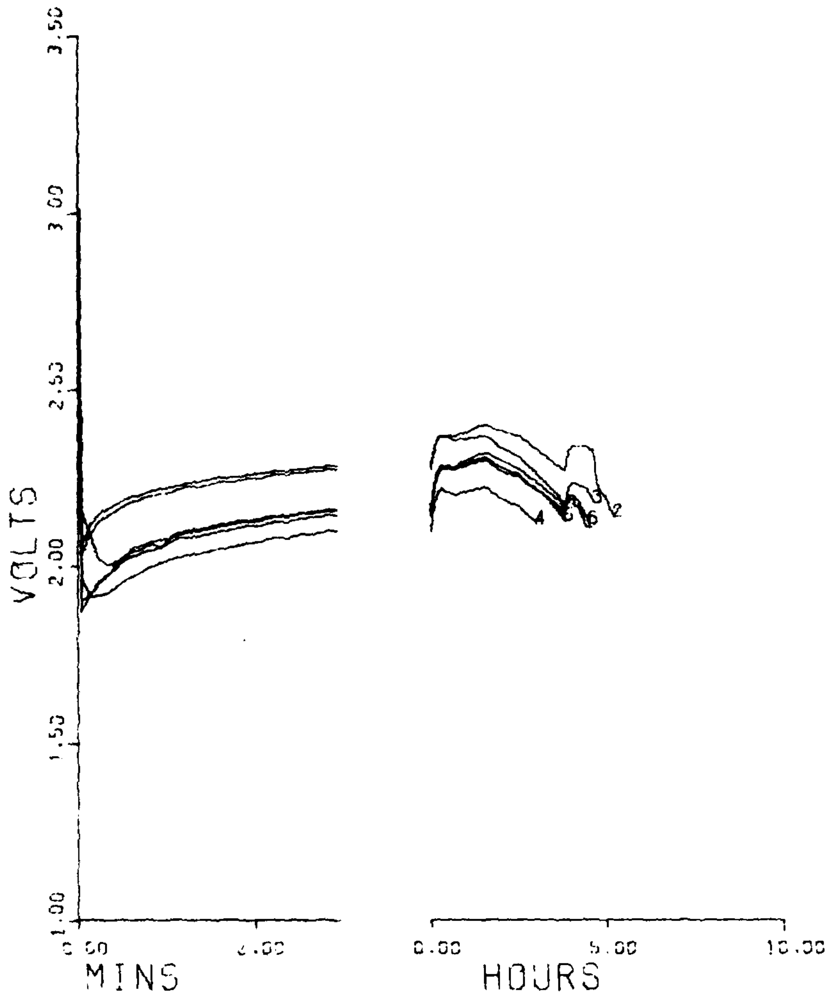

Figure C-9. Computer Plot - HW: .6D LI-SO2 Cells
HTS: 5 Months: 300 MA DISCH At -40 F

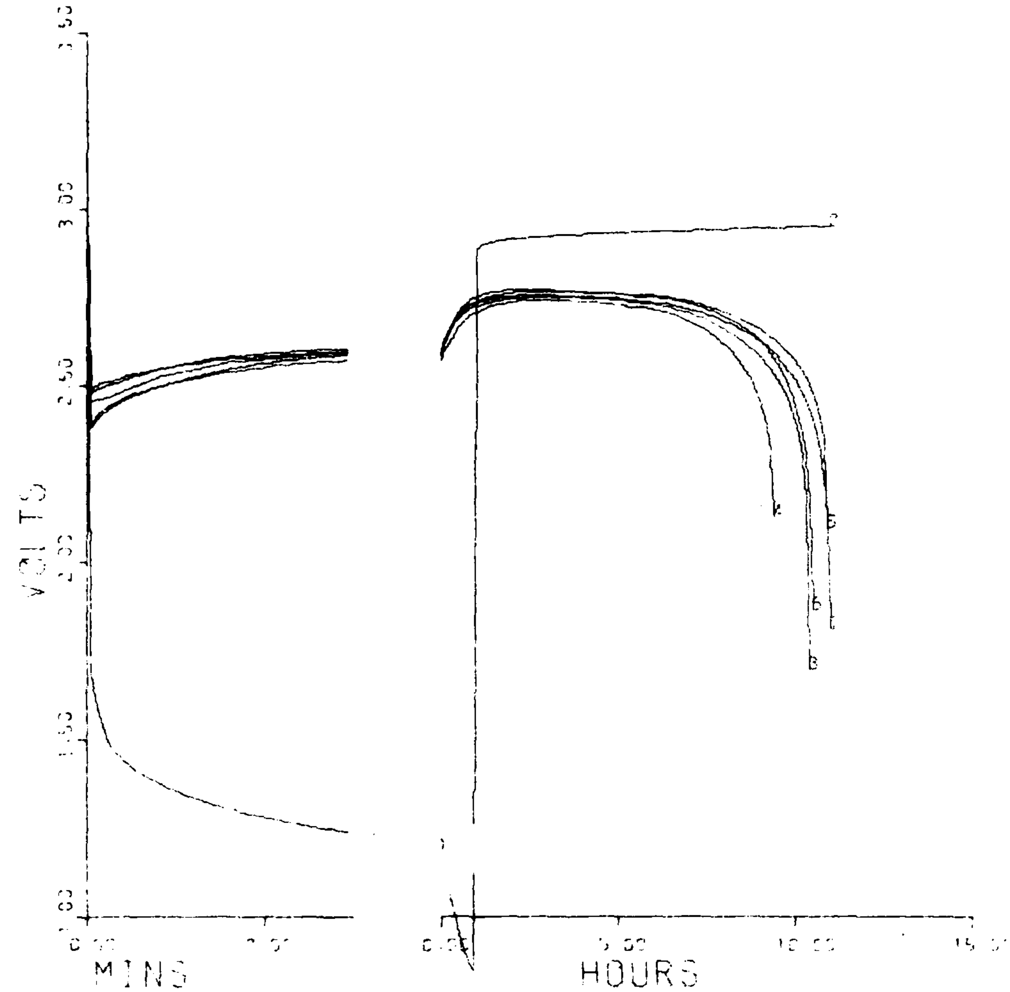

Figure C-10. *Computer Plot - HW .6D LI-SO2 Cells*
HTS: 6 Months: 300 MA DISCH At 70 F

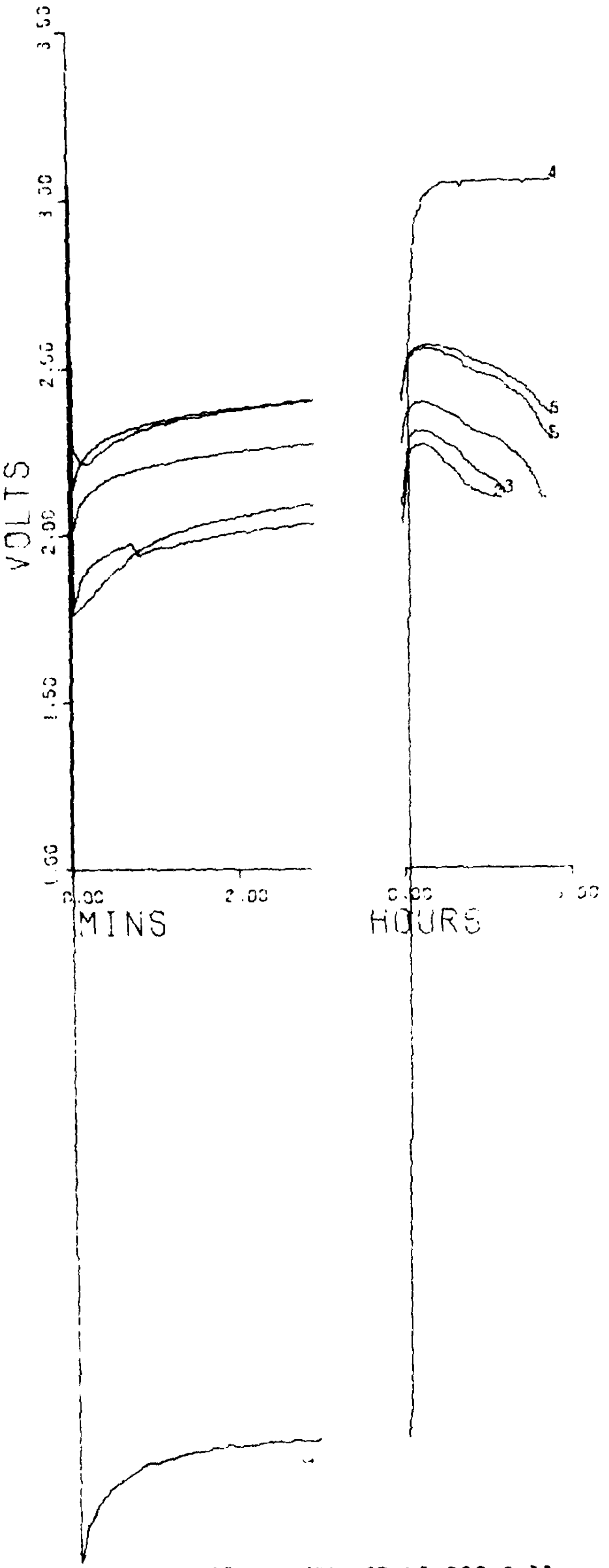

Figure C-11. Computer Plot - HW .6D LI-SO2 Cells
HTS: 6 Months: 300 MA DISCH At -40 F

AD-A119 374 AIR FORCE WRIGHT AERONAUTICAL LABS WRIGHT-PATTERSON AFB OH F/G 10/3
TESTING OF AN IMPROVED LITHIUM-SULFUR DIOXIDE BATTERY FOR AIRCR--ETC(U)
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UNCLASSIFIED AFWAL-TR-81-2137 NL

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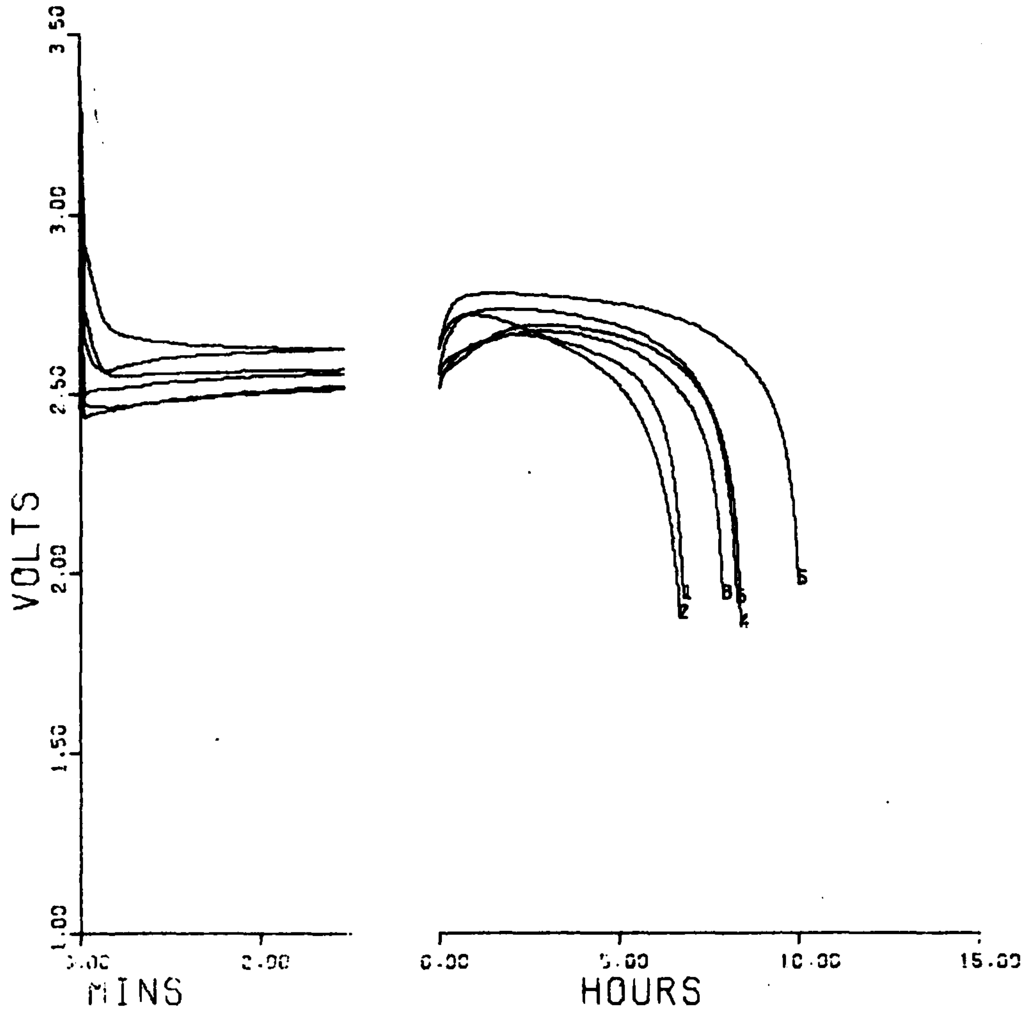

Figure C-12. Computer Plot - HW .6D LI-SO2 Cells
HTS: 7 Months: 300 MA DISCH At 70 F

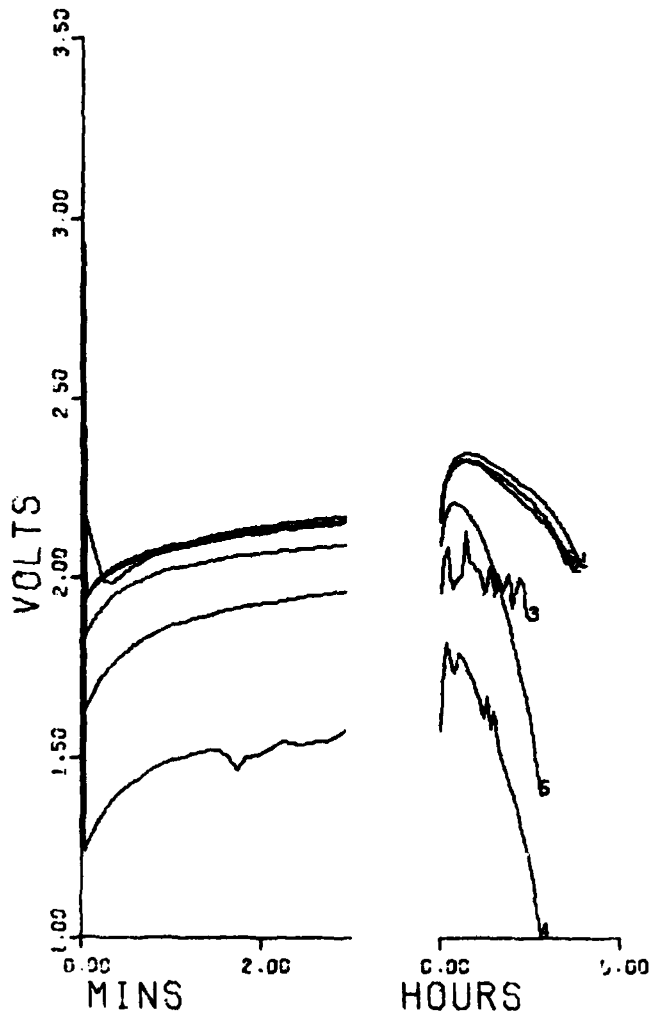

Figure C-13. Computer Plot - HW .6D LI-SO2 Cells
HTS: 7 Months: 300 MA DISCH At -40 F

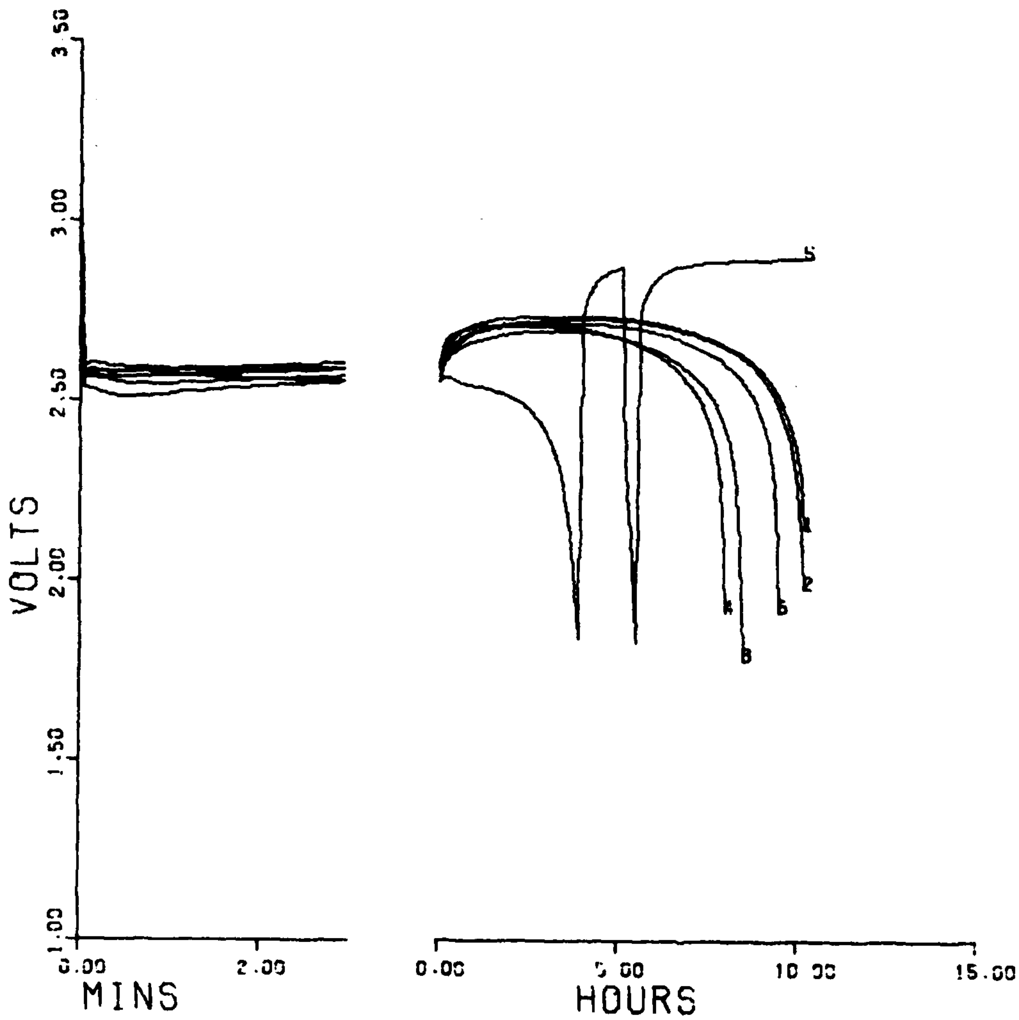

Figure C-14. Computer Plot - HW .6D LI-SO2 Cells
HTS: 8 Months: 300 MA DISCH At 70 F

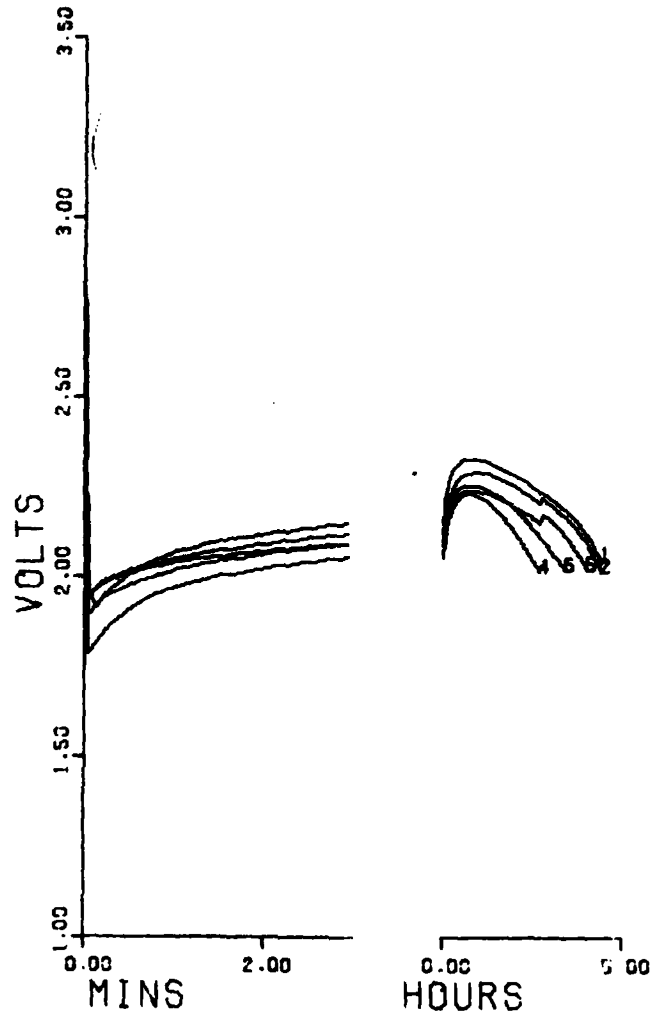

Figure C-15. Computer Plot - HW .6D LI-SO2 Cells
HTS: 8 Months: 300 MA DISCH At -40 F

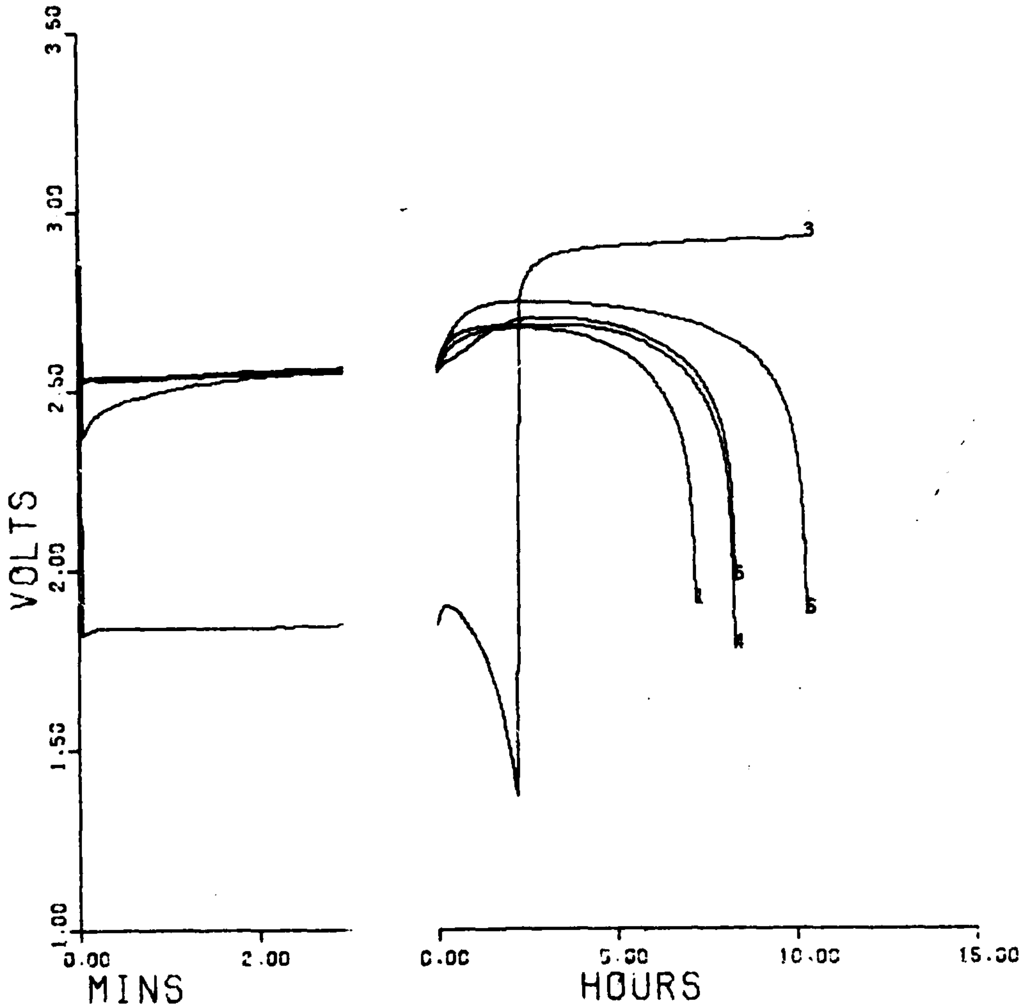

Figure C-16. Computer Plot - HW .6D LI-SO2 Cells
HTS: 9 Months: 300 MA DISCH At 70 F

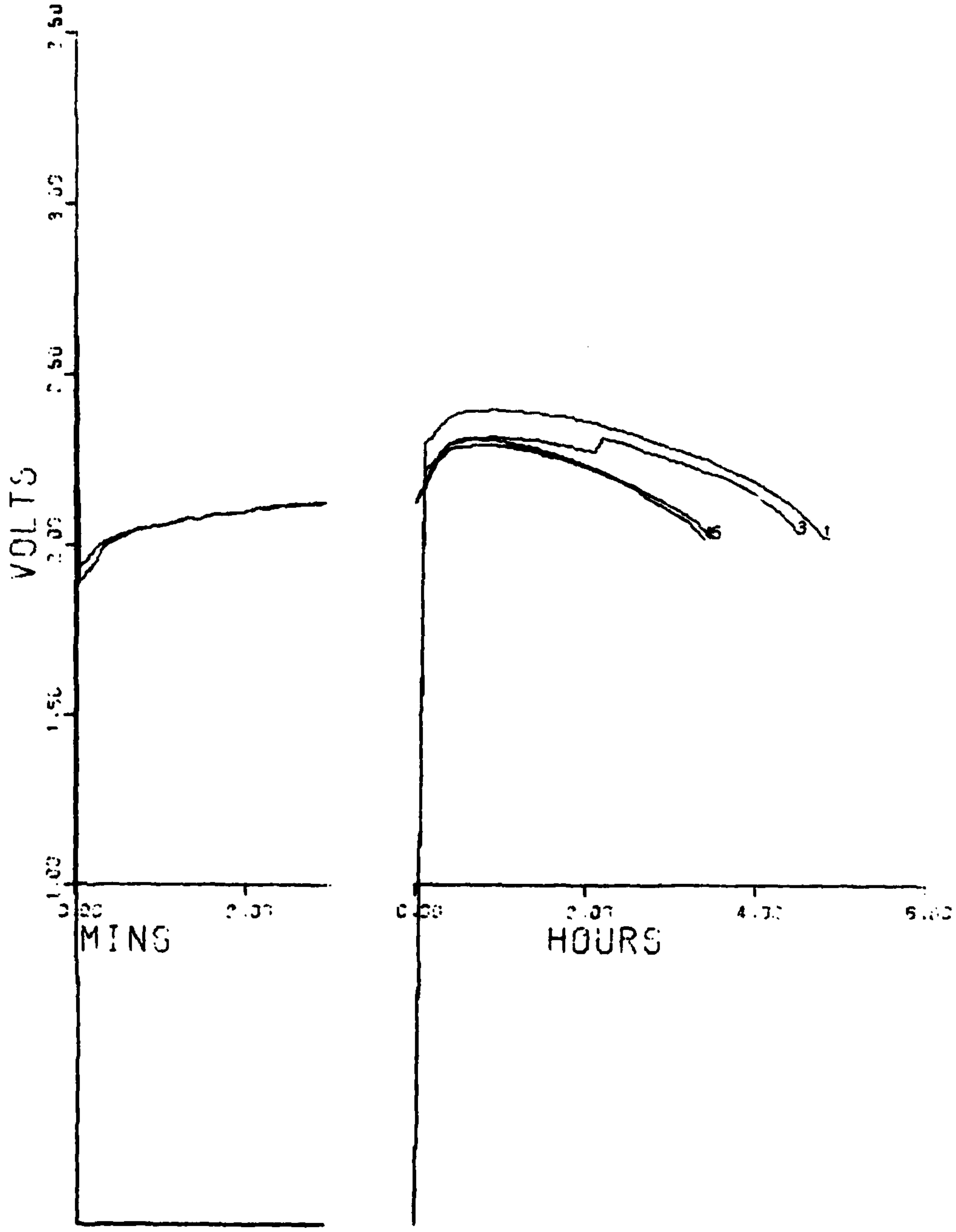

Figure C-17. Computer Plot - HW .6D LI-SO2 Cells
HTS: 9 Months: 300 MA DISCH At -40 F

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